

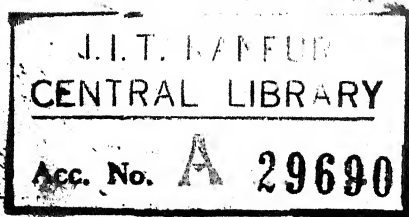
# **STUDIES ON COAGULANT COMBINATIONS IN CONCENTRATING ALGAE**

**A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY**

**By  
RAMALINGAIAH**

**to the**

**DEPARTMENT OF CIVIL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
JULY 1974**



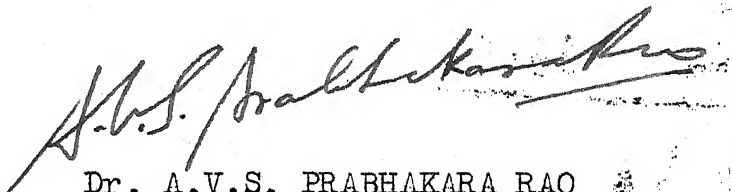
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## CERTIFICATE

This is to certify that the present work entitled "Studies on Coagulant Combinations in Concentrating Algae" has been carried out by Shri Ramalingaiah under my supervision and the work has not been submitted elsewhere for a degree.



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## SYNOPSIS

### STUDIES ON COAGULANT COMBINATIONS IN CONCENTRATING ALGAE

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✓ Stabilization ponds produce 12 to 60 tonnes of algae per acre per year depending on season. Since the concentrations of algae in effluents is low, their size being small, concentrating them was difficult. Concentrations and cost of chemicals used for normal coagulation and flocculation were reported to be high.

A study of concentrating algae using combinations of chemicals was made. It was found that dose of individual chemicals can be reduced when used in combinations. ✓ Using sulphuric acid to bring the pH to 6 reduced the alum concentration from 500 mg/l to 300 mg/l to give 85 per cent algae removal. Nirmali seed extract (2 mg/l) with filter alum (1000 mg/l) gave 80 per cent removal. When cost of the chemicals used per Kg dry weight of algae was compared it was found that lime (500 mg/l) and nirmali seed extract (1 mg/l) combination was least expensive Rs 1.75, followed by lime (250 mg/l) and ferric chloride (60 mg/l) Rs 2.06. ✓ While combinations of chemicals bring down the doses needed for the same amount of concentration of algae, it is concluded that further study is needed to find out the toxicity or otherwise of the harvested algae that can be put to some use like digestion or animal feed. ✓

## CHAPTER I

### INTRODUCTION

Pollution is considered to be a resource, out of place. With the rapid advancement of the culture of mankind, the world is utilizing the available resources so quickly, that search for alternate sources and resources is taking place all over the globe. Mankind is facing shortage of energy, food, and sufficient water. Utilization of pollutants for some basic purposes is a part of this search. A material is considered to be a waste only when there is no immediate use for it in that environment. If the pollutant can be gathered from the waste effluents and used, it would solve both the problem of pollution as well as resource.

In order to meet any problem on long term basis, constant supply of raw material is a must. Thus the primary energy catchers of sunlight, the plant kingdom, should be the ideal sources for solving energy problems. Even though other physical or chemical or electronic devices can be used for solar energy conversion, these cannot replace plant life since they have more than a single role to play, like fixing carbon dioxide, releasing oxygen, forming the primary producers of the food chain. Keeping the economics of a process within the reach of common man should be one of the constraints of any solution. In the last few years researchers in the field of environmental pollution control are experimenting on harvesting and utilization of algal cells which grow abundantly in the waste stabilization

ponds. A properly maintained pond is expected to yield 12 to 60 tonnes of algae per acre per year depending on the season and place. Algae, the primary plant, can be used for various purposes as cited later in the literature. Most important of the uses could be to supplement food or fodder and existing energy sources, per each pound of volatile matter fed to a digester in the form of algal slurry yielded 7.0 cubic feet of gas under certain loading rate and detention time and the gas contained 60 per cent of methane and had a net fuel value of 968 BTU/Ft<sup>3</sup>. Moreover, algae did not need external supply of nutrients for digestions.

These facts make it very attractive as energy sources. However, it was found that algal sludge obtained by chemical coagulation using alum was not digestable. Aluminum sulphate is known to be poisonous to germinating seeds of peas, wheat, as well as to fish. Aluminum sulphate also has bactericidal, and viricidal effects. Thus there is a need to reduce the concentration of alum or replace it by some other chemical, in concentrating the algae from the pond effluents either for use as food/fodder or energy source. A number of synthetic polyelectrolytes have become popular in water treatment and more recently in waste treatment systems. The use of these compounds reduce the coagulant dose considerably and achieve, simultaneous, better results. However, whether they are toxic to micro and macro organisms is not clear. Normally, the naturally occurring materials could be biodegraded with or without acclimated microorganisms. Chemicals like ferric chloride are



reported to be toxic to fish only due to the pH change they bring about when used. Similarly organisms tolerate calcium ions if the pH is not too high.

Thus it is felt that information on reducing the dose of alum may serve in reduction of cost and toxicity. Since work with polyelectrolytes had shown that combination with alum they increased the efficiency, an attempt is made in this study to find out chemicals that can act together in concentrating the algae that are expected to be used mainly for gas production.

The aim of the present work can be stated to be, to find that best combination of coagulents and coagulant aids under natural conditions of environment and work out the feasibility of concentrating algae from quality and cost aspects.

## CHAPTER II

## LITERATURE REVIEW

2.1 GENERAL INFORMATION ABOUT WASTE STABILIZATION PONDS

The first waste stabilization pond came into existence in 1924 at Santha Rosa, California, U.S.A. (3). In their relatively short period of history, waste stabilization ponds have been referred to by many different names such as oxidation ponds, redox ponds, maturation ponds, sewage lagoons, anaerobic lagoons, facultative lagoons (1,2). The use of waste stabilization ponds in India is virtually unrecorded historically. The village tank which invariably receives pollution and is commonly green can be considered as an example of the early use of stabilization ponds in the country (2). The first waste stabilization pond designed on the basis of certain empirical criteria, came into existence in this country, in 1957 at Madras in the University campus. Ponds for treatment of industrial wastes combined with domestic wastes were built at Bombay and other places (2). There are now over 50 ponds in operation in India and are receiving increasing attention because of their simplicity in construction, operation and maintenance (2).

2.1.1 Classification of Waste Stabilization Ponds

The waste stabilization ponds are classified according to the biological processes taking place, namely, Aerobic,

Anaerobic, Hetro-aerobic (Amphi aerobic) or Facultative (2,4).

Aerobic ponds in which suspended and dissolved substances are stabilized by aerobic microbic populations supplied with needed oxygen by algal photosynthesis as well as by gas transfer at the pond surface (4). Aerobic ponds are shallow in depth varying from 0.3 meters to 1.5 meters (2). These ponds perform three functions: (i) they effectively stabilize the organic wastes, (ii) reclaim the waste matter as saleable algae, and (iii) produce effluent of good quality with a minimum of algal nutrients remaining. Disregarding phosphorous, sulfur and trace elements, the oxidation of organic matter was found by Oswald et al (5-7) to follow the following reaction:



In aerobic oxidation ponds, BOD reduces up to 80 to 90 per cent, ammonia nitrogen 75 to 90 per cent, organic nitrogen up to 60 per cent, phosphorus up to 96 per cent and potassium up to 10 to 20 per cent (1,8).

The anaerobic ponds are described by Parker et al (9) in detail. Degradable substances are stabilized by anaerobic microbic populations in the continuous absence of dissolved oxygen (4). These ponds are designed for higher organic loadings so that photosynthetic algal action preclude and anaerobic conditions prevails through out the pond (2). Anaerobic decomposition degrades organic matter in various steps, the end products being methene, carbon dioxides. The normal depths of anaerobic ponds vary from 2.5 meters to 3.7 meters (2).

The effluent from this pond will have a high BOD and requires further treatment (2).

Facultative ponds are the most common type of waste stabilization ponds. These ponds are predominantly aerobic at the top layers during sunshine hours, the bottom layers being generally anaerobic (10). Van Heuvelen has described the facultative ponds in detail (11).

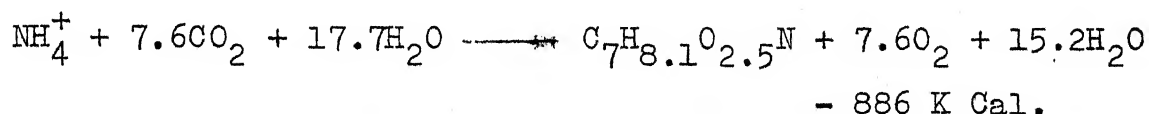
#### 2.1.2 Mechanism of Stabilization of Organic Wastes

The mechanism of stabilization of organic wastes in the stabilization ponds depends on the algal bacterial symbiosis (6), each producing end products, which are useful to the other. Under suitable conditions saprophytic, micro-organisms oxidise organic matter into carbon dioxide, ammonia, phosphate etc. The end products which are liberated by bacterial population happen to be the nutrients for algae. In presence of sunlight and the carbon dioxide given out by bacteria, or dissolved from atmosphere, photosynthesis will take place, in which process the algae produce oxygen and synthesise more algal cells (12). The oxygen liberated by algae is directly utilized by the bacterial population to oxidise the organic matter present in the wastes. The excess quantity of bacteria and algae produced in algal bacterial symbiosis flows out with the effluent. Out of the total oxygen produced by the algae in photosynthesis, a fraction of it is consumed by themselves for respiration

purposes. Normally in aerobic ponds the production of oxygen is many times more as compared to algal respiration.

### 2.1.3 Photosynthesis and Energy Conversion

In waste stabilization ponds, during day time, algal photosynthesis is the major source of oxygen for aerobic oxidation. The oxygen supplied by atmospheric reaeration is very small and may be neglected (13). Oswald (5) gave the following equation for composition of algae:



One milligram of algae synthesised through photosynthesis will produce roughly about 1.67 mg of oxygen (6).

Bhopardhikar (14) reported that the earth receives 20 million K Cal of solar energy on an acre of land each day. Out of which  $\frac{1}{2}$  of the total radiation energy is composed of heat rays and infra-red rays which are not effective in photosynthesis. The plant is capable of utilizing half of the incidental solar energy. The average solar energy on the subcontinent of India is of the order of 400 Langleys per day and this solar energy is available in all the season of the year.

Only a small fraction of solar energy received on a pond surface is converted into chemical energy and gets fixed in new algal cells. For per milligram of algal synthesis, the solar energy required is about 6 calories.

## 2.2 CONCENTRATION OF ALGAE IN PONDS (YIELD)

The yield of algae in waste stabilization ponds may vary from one ton per acre per month in winter to five tons per acre per month in summer as reported by Arceivala et al (2). The yield of algae is dependent on the climatological conditions.

### 2.2.1 Different Species of Algae

The species of algae in waste stabilization ponds vary from season to season. Raschke (15) reported that green flagella algae dominated in winter and spring, green algae in summer. Singh et al (16) reported that sewage in Uttar Pradesh (U.P.) contains 28 species of cyanophyta, 13 of chlorophyta, 17 of bacillariophyta and euglenophyta. Most diatoms were observed during monsoon season. Sahani 'Arun' (17) observed the following species of algae in I.I.T. campus waste stabilization pond at Kanpur.

#### I. Green algae (chlorophyta)

- (i) Chlorella, (ii) Chlamydomonas,
- (iii) Micractinium

#### II. Blue-green algae (cyanophyta)

- (i) Anabeana, (ii) Anacystis, (iii) Orthospira

#### III. Diatoms (bacillariophyta)

- (i) Navicula

#### IV. Flagellates (euglenophyta)

- (i) Euglena

### 2.2.2 Use of Algae

As reported in literature (14,18) algae generally contain ten amino acids, 50 to 60 per cent of protein, 20 to 30 per cent of lipids and 10 to 20 per cent of carbohydrates. The algae also contain 5000 I.U/gm of dry weight vitamin A, 4 I.U/gm of dry weight vitamin B<sub>1</sub>, 9 I.U/gm of dry weight vitamin B<sub>6</sub>, 2000 I.U/gm of dry weight vitamin C.

Because of the likely presence of pathogens, sewage grown algae might not be suitable for human consumption but they can be used as chicken and live-stock feed (19). It can be also used as fertilizer (20) or as fuel, by producing methane through anaerobic digestion (21,22).

### 2.3 METHODS OF COLLECTING THE ALGAE

Collecting the algae from waste stabilization pond effluent is difficult due to their low concentration, low specific gravity and microscopic physical size. However many workers tried by different methods and a brief review of their work is given in the following pages.

The processing of algae involves three steps (23)

- (i) Initial concentration of algal cells from waste stabilization pond effluent
- (ii) Dewatering of concentrated slurry
- (iii) Drying the dewatered slurry for further use.

The above mentioned three steps are necessary to bring algae to a finished stage, as no single step can bring it into a finished stage for further use. After dewatering the

slurry about 8-15 per cent solids content can be achieved.

Some methods tried by different workers for collecting algae can be grouped into three major groups as follows,

- (1) Physical Methods
- (2) Chemical Methods
- (3) Biological Methods

### 2.3.1 Physical Methods

Physical process of concentration of algae includes the following methods:

- (1) Centrifugation
- (2) Ion exchange
- (3) Passing through charged zones
- (4) Microstraining
- (5) Filtration
- (6) Ultrasonic vibrations.

#### 2.3.1.1 Centrifugation:

Experimental study conducted by Oswald and Golueke (23) showed that the harvesting of algae from algal suspension of 200 mg/l, varied almost linearly as the through-put rates were increased from 100 to 385 gpm, varying from 80 to 90 per cent removal at 100<sup>gpm</sup>/<sub>2</sub> to 60 per cent removal at 385 gpm, at rotational velocities 3000 and 3300 rpm respectively. It was observed that the disc angle of the centrifuge also affects the separation higher than 300 gpm. At 385 gpm the removal at disc angle of 55° was 10 per cent greater than that with the disc angle at 45°. The field study made by Golueke and



Oswald (23) showed that the power required per tonne of dried algae, at 200 mg/l concentration, ranged from 3300 KWH at a rotar speed of 3000 rpm and through-put rate of 200 to 300 gpm to 6200 KWH at a rotar speed of 3300 rpm and a through-put rate of 100 gpm. The power consumption is increasing with the increase in rotar speed. The power consumption inversly varied with algal concentration. They have further said that out of the many method tried for the accomplishment of the harvesting of algae, centrifugation seem to be the best method, because of it's simplicity in operation and harvesting of algae without using any chemicals. But the power consumption, the cost of the centrifuge and the limited capacity of the centrifuge, made centrifugation very costly process.

#### 2.3.1.2 Ion Exchange:

Golueke and Oswald (23,24) reported that algae could be removed by passing an algal suspension through a column either of strong or of weak cation exchanger. The mechanism of removal apparently involved a flocculation that resulted from changes in surface charge of algal cells brought about by charge of the resin. This was demonstrated by the failure of the exchange column to remove algae after their exchange capacity had been exhausted. The removal ability become less after each regeneration of the column. The draw back of the process was that the regeneration of columns could be accomplished only with  $H^+$ . The addition of  $Na^+$  or any cations other than  $H^+$  effectively interferred with algal removal capacity. The exchange efficiency of the resin with respect to

algae is only 15 per cent of that with respect to ions (24). Further more studies would be necessary to find out the suitability of this process for field scale size.

#### 2.3.1.3 Passing through Charged Zones:

The possibility of using the negative charge of algae, to cause them to migrate to the cathode of an electrolytic cell was tried by Golueke and Oswald (23). They used aluminium, copper, and carbon electrodes either in pairs of the same material or of different materials. The distance between the electrodes varied from  $\frac{1}{8}$  to  $\frac{1}{12}$  inch and current varied from 0 to 900 milli ampere. Excellent separation occurred when aluminium or copper electrodes were used, with through-put rates varied from 0.05 to 1.2 gpm per ft<sup>3</sup>. Excellent separation occurred with aluminium or copper electrodes because of good floc formation by the release of copper or aluminium and subsequent formation of hydroxides of copper or aluminium. When carbon electrodes were used very little separation was observed. Recently Treharne, et al (25), reported that, potential between a pair of electrodes immersed in polluted waste water with 15 volts and 15 milli ampere over 72 hours completely removed the algae.

#### 2.3.1.4 Microstraining:

The experimental report of Golueke and Oswald (23) revealed that the experiment for in flow rates varied from 187 to 378 l/minute at the microstrainer rotation speed of 10, 20 and 30 rpm, the algal removal was extremely low. Even with the addition of filter aids and decrease in flow rate, the efficiency of removal with microstrainer was not improved. Berry (33) reported that filamentous algae could be removed by

microstrainers but removal of planktonic forms not at all improved.

#### 2.3.1.5 Filtration:

Golueke and Oswald (23) attempted filtration on laboratory model by using a buchner funnel and with an oliver leaf of 3 cms in diameter. The filter media tried by them were, paper, cloth, fine mesh, filter paper, nylon, cotton and woolen screens, with filter aids such as diatomaceous earth, corn meal, corn starch and calcined rice hulls. It was reported that in the absence of filter aids, all filter media including fine mesh, cotton and woolen screens, nylon screens were ineffective. Biological filters were effective but the through-put rate was far lower than the minimum required for practical application. Studies of Sinha (26) on filtration concludes that sand filter was uneconomical, because of the necessity of frequent backwashes.

#### 2.3.1.6 Ultrasonic Vibrations:

It was believed that if algal cells were compelled to come in contact with each other by some force and thereby have their surface charges neutralized, they then would adhere to each other. Eventually they might build up clumps of algal cells sufficiently large enough for settling, then they can be removed by conventional methods. The experimental results of Golueke and Oswald (23) showed that the algal cells instead of being clumped together, the algal cells were dispersed effectively at the frequencies of 1500 cps and above.

### 2.3.2 Chemical Methods

Chemical methods of collecting algae includes the following methods:

(i) Flotation, (ii) Coagulation and flocculation.

#### 2.3.2.1 Flotation:

The principle of flotation of waste water treatment has been described in detail by Rich (27). Golueke and Oswald (23) tried flotation method for collecting algae, by using 18 different flotation reagents. Appreciable concentration of algae obtained only with two reagents, and even with these two the extent of removal was too small to be practical. Levin et al (28,29) reported that flotation method in which the algal concentration of the harvest is a function of pH, aeration rate, aerator porosity, feed concentration and height of the foam in the processing column. The critical pH level for flotation of algae was 4.0. J.M. Barnes et al (29) investigated on flotation of algae in laboratory as well as in sewage lagoons. They observed that at pH 3 and at pH 12, the per centages of removal were same. From the studies of Ramachandran (30) conducted on foam flotation in batch process by using imported cat ionic surfactant, hexadecapyridinium chloride ( $C_{21}H_{38}NCl$ ), observed that 75 per cent removal of algae was achieved with surfactant dose of 20 mg/l, air flow rate of 1.5 VVM and pH 3. Kumara Sastry (31) also used foam flotation for algal harvesting on continuous process with hexadecapyridinium chloride as surfactant. He obtained similar results with a dose of 20 mg/l. In addition to

hexadecapyridinium, Sastry (31) tried with indigenous surfactants such as Acinol CDMB, Acifix liquid, Dex 2, Saponin etc. but the results were very poor and was not comparable with the results of hexadecapyridinium chloride.

The cationic surfactant hexadecapyridinium chloride, even though gave good removal, but because of it's high cost and nonavailability in this country, reduction of pH of the suspension as low as 3.0, and aeration of the system made this process very expensive.

#### 2.3.2.2 Coagulation and Flocculation:

Removal of algae can be achieved through coagulation and flocculation involving the additions of coagulents such as aluminium sulphate (alum), ferric chloride, lime, or organic flocculants, acids etc. Coagulation is induced by addition of coagulants, followed by a brief period of rapid mixing and ten to fifteen minutes slow mixing to develop floc particles of sufficient size and to permit rapid sedimentation.

Golueke and Oswald (23) observed that very little precipitation occurred at pH levels from 9.5 to 10.5, where as at pH 10.6 most of the algae was removed from the suspension. A dose of 40 mg/l ferrous sulphate and 120 mg/l of lime gave a removal of 86 per cent of algae. They observed that using alum maximum removal of algae from suspension at pH level 6 to 6.8 with a dose of 70 mg/l. About pH 7, the removal efficiency decreases.

Sinha (26) reported that 92 per cent of algal removal was observed with alum dose of 400 mg/l with pH adjustment to 7 prior to addition of alum, without adjustment of pH for the same per cent removal, 900 mg/l of alum was required at pH 8.7.

Saini (21) also reported that without pH adjustment 2000 mg/l of alum was required to achieve 89 per cent removal when initial concentration of algae was 525 mg/l. By adjusting the pH to 7 the quantity of alum required for the similar removal was only 1000 mg/l.

Golueke and Oswald (23) have further said that the use of organic reagents 'Sondelite', purifloc 601 and 602, gave better results. All above electrolytes belong to cationic polyelectrolytes.

Van Vuuren and Van Duuren (32) reported that Dowseparan NP10, and wispro floc 20, with doses varying from 0.5 to 2.5 mg/l combined with alum gave better results.

The studies of Megarry and Tongekasane (33,34) reported that number of cationic polyelectrolytes tried in their experiment, only Alfloc 980, C 3, PEI 1090 and purifloc C 31 were observed to aid significantly the flocculation of algae using alum.

Jerse M. Cohen et al (35) also reported that 99 per cent removal of algae was observed with a dose of 20 mg/l of cationic B polyelectrolytes in his studies on natural and synthetic polyelectrolytes as coagulant aids.

Irwin and McCarty (36) have reported that cation toxicity is some sort of interaction between cations and enzymes, while toxicity results when the enzyme units with an improper cation. McCarty (37) further reports that lime and magnesium hydroxide could be used up to 10,000 mg/l, and 6500 mg/l  $\text{Na}^+$  can be tolerated, provided pH maintained at 7 without any harmful effects on the anaerobic digester.

### 2.3.3 Biological Methods

Under this heading two methods of collecting algae are given:

- (i) Auto flocculation
- (ii) Bioflocculation

#### 2.3.3.1 Auto Flocculation:

Golueke and Oswald (23) during their studies on algal harvesting observed a natural separation process which took place under certain conditions. The phenomenon consisted of a naturally caused precipitation and settling of algae. The necessary conditions for autoflocculation are as follows:

- (i) An actively photosynthesizing shallow culture of algae
- (ii) A relatively warm day, and
- (iii) Sunlight.

In this process they observed, that all the algae settled down to the bottom of the pond. Even though this process is simple it necessitates the use of large number of ponds, which is uneconomical. However this hypothesis require more studies to find out the suitability for field application.

### 2.3.3.2 Bioflocculation:

Tenny and Stumm have proposed that the aggregation of microorganisms in biological waste treatment results from the interaction of polymers which are either excreted by microorganisms or exposed at the surface of cells as reported in reference (38). Pavoni (39) reported that polymer production of bacteria has a direct correlation between polymer production and biological flocculation with maximum agglomeration occurring during endogenous growth stages. Many workers have postulated an algal bioflocculation. Pavoni et al (40) have developed a sound model for algal flocculation. Moore (41) in his study showed that extracellular polysaccharide produced by eight species of green and blue green algae ranges from 174 mg/l to 557 mg/l. Most of the polysaccharides are composed of four monosaccharides; a hexose, a pentose, a methyl pentose and and uronic acid. Robert et al (42) reported that algae excretes two types of polymers such as, capsule material associated with certain diatoms that include many blue green and green algae. The other type of polymer consists of those which diffuse into the medium from cell, the best known of these is chlorellin produced by certain species of chlorella. Fogg et al (43) observed that algal cell contain about 7 mg of  $N_2$ /l and 0.15 mg of  $\alpha$ -amino nitrogen/l.

Pavoni et al (40) postulated that the algal agglomeration appears to be governed by the physiological state of the microorganisms. Algal flocculation was not observed to occur



until the microorganisms had entered into a endogenous growth phase. Mechanism of bioflocculation of algae seem to be resulting from the interaction of high molecular weight exocellular polymers, which have sufficiently accumulated on the surface of the cells in the endogenous phase. These polymers electrostatically or physically bond and subsequently bridge the cells of the dispersion into a three matrix of sufficient magnitude to subside under quiescent conditions. The recent studies of Sahani 'Arun' (17) reported that bio-flocculation could be induced by blending with some portion of algal suspension and mixing this blended portion to unblended algal suspension in a particular ratio. The efficiency of removal increases with the increasing in algal concentration. The per cent removal was directly proportional to blending.

## 2.4 NATURAL POLYELECTROLYTES

(i) Nirmali Seed, (ii) Crotalaria Seed.

### 2.4.1 Nirmali Seed (Strychnos Potatorum)

The use of nirmali seed for water clarification is not new, as it has been mentioned in Sanskrit literature (35), dating back to 2000 B.C. The nirmali seed belongs to the group of Strychnos potatorum, Linn, commonly known as clearing nut or nirmali seed. Strychnos potatorum is one of the group of trees which grow profusely in various parts of India and South-East Asia (44). Nirmali seeds are available abundantly in Chanda district, Maharashtra State, where local

people use this for removing turbidity of muddy water (44). The seeds have the property of clarifying foul and muddy water. The seeds are nontoxic and in fact have been recommended as medicine for diarrhoea, irritation of urinary organs, and suppression of boils (44).

Sen and Bulusu (45) have reported that nirmali seed contains strychnine and albumin, brucine and galactomannan residue similar to ghargum. Further they have said that the coagulation was due to the presence of strychnine and albumin.

Rao and Sastry (47) have observed by their studies, that nirmali seed paste contains a weak negative charge and the seed contains albumin, brucine and not strychnine.

Further from the studies of Dhekney (44), Sen and Bulusu (45), Bulusu and Sharma (46), Rao and Sastry (47), it has been observed that nirmali seed fails to act as coagulant but it acts as a coagulant aid. They observed that the nirmali seed extract serves as an effective coagulant aid to all the conventional metal coagulents. A dose of 1 to 2 mg/l of the extract reduced the amount of metal coagulant required to  $\frac{1}{3}$  to  $\frac{1}{2}$  without affecting the efficiency of turbidity removal. It was further observed that nirmali seed alone did not remove bacteria in water treatment (44).

#### 2.4.2 Crotalaria Seed

The crotalaria seed belongs to the family of papilionaceae of Leguminosae cultivated in South India, a green erect herb, branched or unbranched with yellow flowers. The green leaves used mainly as animal fodder, remaining portion

of the plant is used or cultivated for green manure. So far no work has been reported on this as a coagulant or coagulant aid, but in the present work an attempt was made.

## CHAPTER III

## MATERIALS AND METHODS

3.1 ALGAL CULTURE IN THE LABORATORY

Since the oxidation pond in the field stopped functioning, a laboratory scale oxidation pond made up of 18 gauge galvanized iron sheet was used. The dimensions of tank being 107 cms x 53.5 cms x 76 cms, providing a surface area of 5724.5 sq cms. The pond was kept outside the laboratory in sunlight. The tank was filled with tap water along with other nutrients, which are essential for the growth of algae. The seed for the oxidation pond set up was from the campus oxidation pond. The tap water analysis is presented in Table 1. For lifting and recirculation purpose compressed air was used. The recirculation was allowed through 3 reactors, the main function of reactors and recirculation was to expose more algal surface to sunlight, so as to enhance the photosynthesis.

In the first set, the daily feed was 100 mg/l of urea, soda ash 100 mg/l and sodium phosphate 10 mg/l along with water. The other trace elements which are essential for algal growth were supplied by the tap water. The daily increase in algal concentration were measured and presented in the Fig. 2.

In the 2<sup>nd</sup> set, the daily feed was increased from 100 to 200 mg/l urea and 100 to 200 mg/l of soda ash. The

TABLE 1

## Analysis of Tap Water

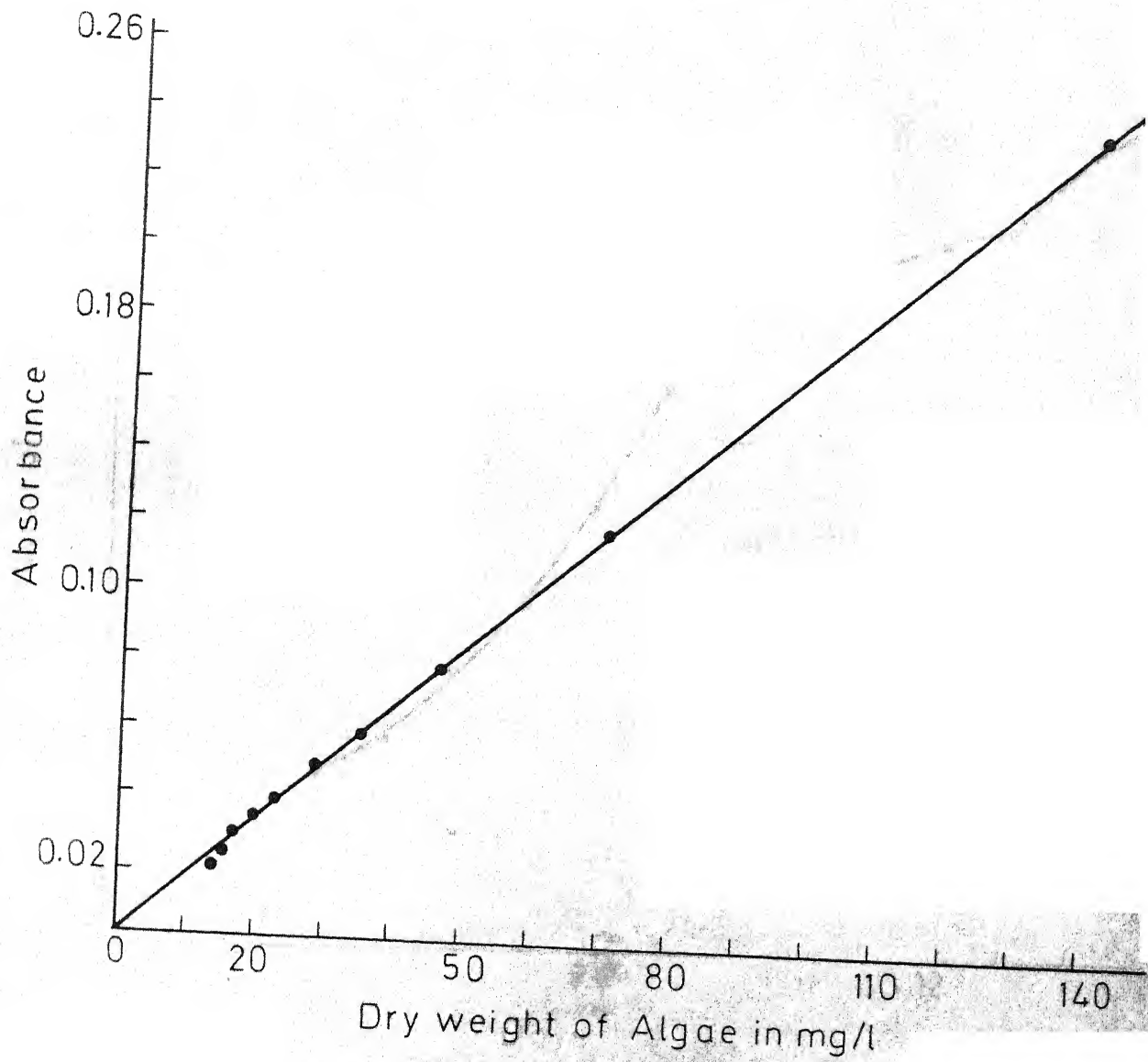
(1)	Temperature	32°C
(2)	pH	7.6
(3)	Total dissolved solids	810.18 mg/l
(4)	Flouride	1.6 mg/l
(5)	Chloride	67.88 mg/l
(6)	Alkalinity	408.0 mg/l as $\text{CaCO}_3$
(7)	Total hardness	170 mg/l as $\text{CaCO}_3$
(8)	Calcium hardness	70 mg/l as $\text{CaCO}_3$
(9)	Magnesium hardness	100 mg/l as $\text{CaCO}_3$
(10)	Calcium	28.0 mg/l
(11)	Magnesium	24.0 mg/l

TABLE 2

## Characteristics of Sewage

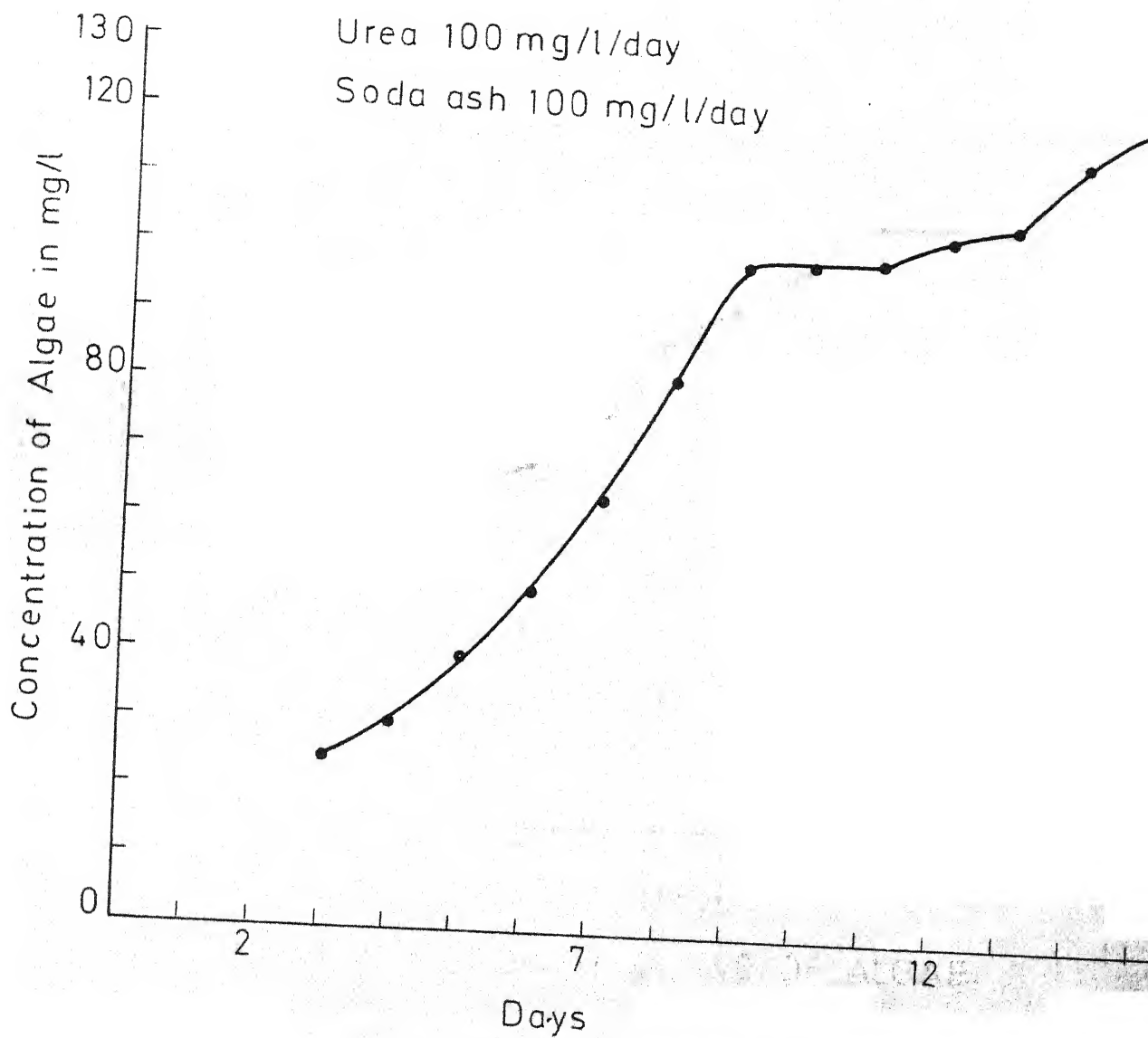
(1)	pH	7.9
(2)	BOD <sub>5</sub> (mg/l)	180
(3)	COD (mg/l)	300
(4)	Suspended solids (mg/l)	120
(5)	Chloride (mg/l)	65
(6)	Ammonia Nitrogen (mg/l)	6.5
(7)	Organic Nitrogen (mg/l)	8.0
(8)	Total Phosphate (mg/l)	5.2
(9)	Alkalinity (mg/l)	460

Optimum wave length 390 m $\mu$   
Path length 1 cm  
Spectronic 20 (Bausch & Lomb)



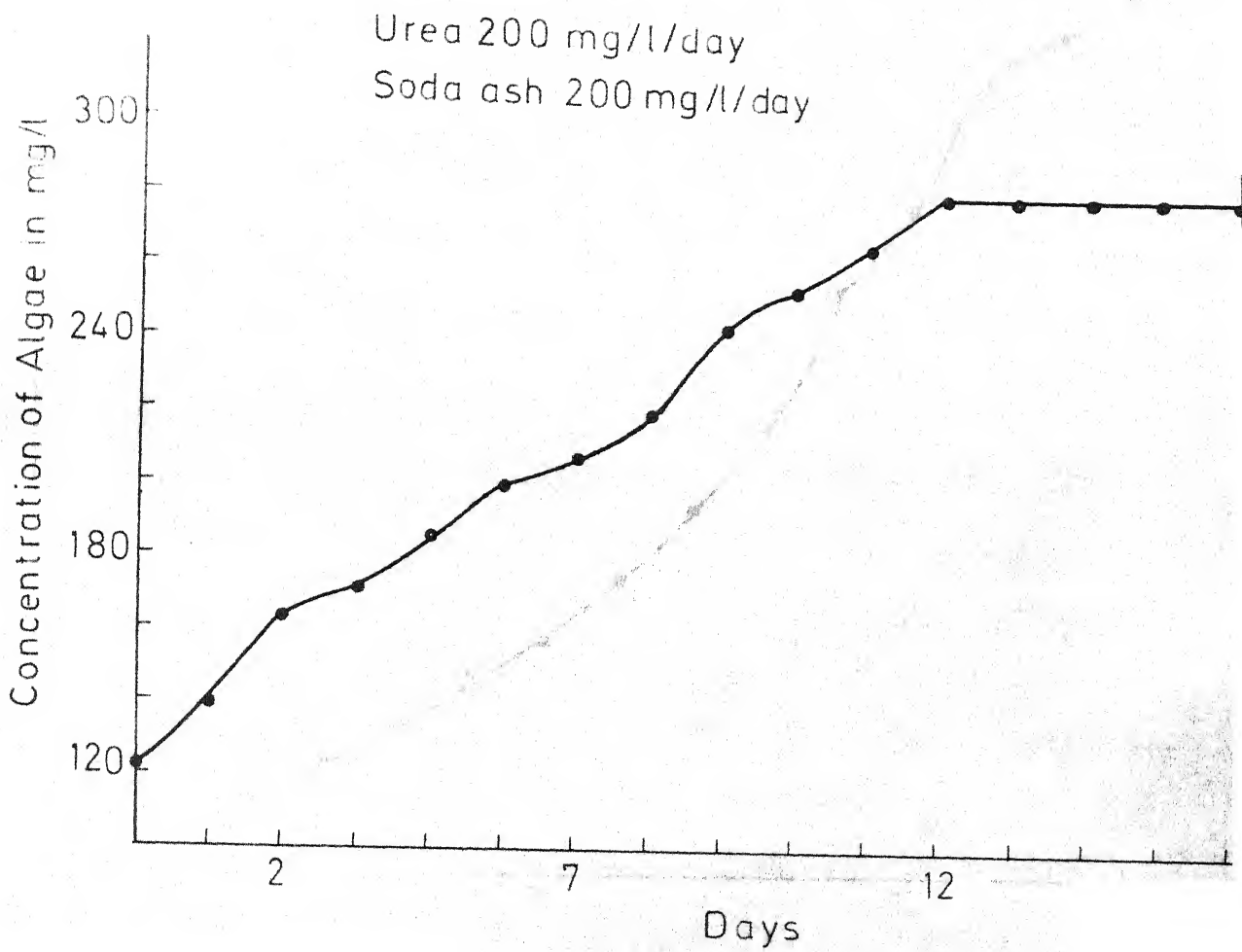
CALIBRATION CURVE

FIG. 1



GROWTH CURVE OF ALGAE

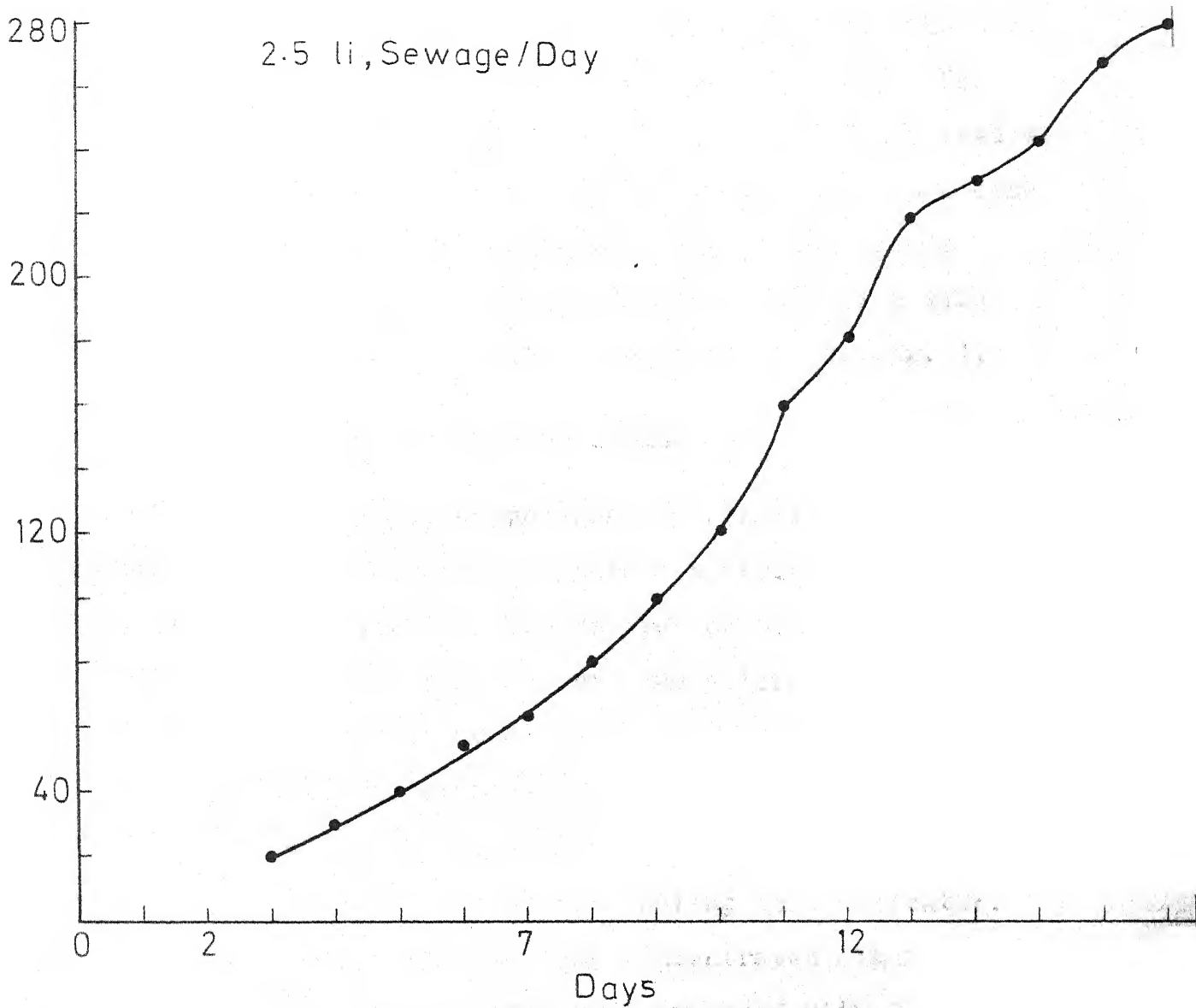
FIG. 2



GROWTH CURVE OF ALGAE

FIG. 3





GROWTH CURVE OF ALGAE

FIG.4

sodium phosphate was only 10 mg/l. The daily algal concentration was measured and presented in the Fig. 3.

The cascade type of apparatus was also set up to grow algae by using raw sewage. The apparatus consisted of two tanks, one at the bottom and the other at the top, these two tanks are connected by a cascade (series of steps). The capacity of this set up was about 50 lit. The daily feed was 2.5 litres of fresh raw sewage. The recirculation was done manually. For the composition of sewage please refer Table 2. The daily increase in algal concentration were measured and a graph was plotted as shown in the Fig. 4.

### 3.2 PREPARATION OF CALIBRATION CURVE

2 liter of algal suspension was centrifuged at 4000 rpm for ten minutes in the laboratory centrifuge (Sorvall SS3). A thick suspension was prepared on 50 ml distilled water by remixing the pellets obtained after centrifugation. 25 ml of the above suspension was taken and filtered through Whatman number 42 filter paper and dried in a hot air oven at a temperature of  $110^{\circ}\text{C}$  for 24 hours. Dry weight of the algal cells was determined after proper cooling in a decicator. With the remaining portion of the concentrated algal suspension different dilutions were prepared with distilled water. The optimum wavelength for algal suspension was found out as 390 m $\mu$  on "Spectronic 20" (Bausch and Lomb) at a path length of 1 cm. Absorbance of each diluted algal suspension was determined at the above wave length. The calibration

curve was drawn with dry weight of algal cells versus absorbance as shown in Fig. 1.

### 3.3 MICROSCOPIC EXAMINATIONS

To identify the species of algae present in the campus oxidation pond and in the laboratory pond, microscopic examinations were carried out and identifications were made according to Standard Methods (48). The species observed during the course of examinations are listed below:

	<u>Campus oxidation pond</u>	<u>Laboratory oxidation pond</u>
(a) Green algae		
(1) Chlorella	Predominant	Predominant
(2) Chlamydomonas	Good in numbers	Good in numbers
(3) Micractinium	Few	---
(b) Blue green algae		
(1) Anabaena	Good in numbers	Good in numbers
(2) Anacystis	Rare	---
(3) Orthospira	Good in numbers	Good in numbers
(c) Diatoms		
(1) Navicula	Good in numbers	Good in numbers
(d) Flagellates		
(1) Euglena	Few	Few

### 3.4 PREPARATION OF EXTRACTS OF SEEDS USED IN THE EXPERIMENT AS NATURAL POLYELECTROLYTES

- (1) Nirmali seed extract (NSE),
- (2) Crotonaria seed extract (CSE)

#### 3.4.1 Nirmali Seed Extract

One gm of nirmali seed powder and 200 ml of distilled

water were mixed in a Bajaj mixer for 10 minutes. Then the suspension was made upto 1 litre by adding distilled water and the extract was kept in a refrigerator till further use.

#### 3.4.2 Crotalaria Seed Extract

Crotalaria seed was grinded into a powder in Bajaj mixer and then sieved through a fine sieve. One gm of powder was taken in one litre of warmed distilled water. The extract was kept in a refrigerator till further use.

#### 3.5 MEASUREMENT OF PROTEIN AND CARBOHYDRATE CONTENTS OF NIRMALI SEED

Protein contents in nirmali seed was determined by using Lowry's method (49). 15 per cent of protein was found in the seed.

Carbohydrates in nirmali seed was determined by phenol sulphuric acid method (49). 53 per cent of carbohydrates was found in the seed.

#### 3.6 MEASUREMENT OF PROTEIN AND CARBOHYDRATES CONTENTS OF CROTALARIA SEED

Protein contents in crotalaria seed was determined by using Lowry's method (49) and was found to be 25 per cent.

Carbohydrates in crotalaria seed was determined by phenol sulphuric acid method (49) and it was 60 per cent.

### 3.7 EXPERIMENTS TO FIND OUT THE IONIC NATURE OF NIRMALI SEED AND CROTALARIA SEED

The nirmali seed extract fail to remove inorganic turbidity in the absence of calcium ions. When  $\text{CaCl}_2$  was added as  $\text{Ca}^{++}$  the removal of inorganic turbidity increases with the increase of  $\text{CaCl}_2$  as calcium. This shows that the nirmali seed extract behaves as anionic polyelectrolyte.

The crotalaria seed extract also fails to remove inorganic turbidity in the absence of calcium ions. When  $\text{CaCl}_2$  was added as calcium, the removal of inorganic turbidity increases with increase in dose of  $\text{CaCl}_2$  as calcium. This seed also behaves as anionic polyelectrolyte.

The inorganic turbidity of canal water was removed by crotalaria seed extract, experimental results are presented in the Table 3. When the initial turbidity was 164 FTU with the dose of 20 mg/l of crotalaria seed extract, removal was 75 per cent of inorganic turbidity in  $\frac{1}{2}$  hour but with the increase in dose reduces the efficiency of removal.

TABLE 3

Dose of Crotalaria Seed Extract V/S Per Cent  
Removal of Turbidity in Canal Water

Initial Turbidity 164 FTU

Dose of crotalaria seed extract in mg/l	Per cent removal in $\frac{1}{2}$ hour
0	10
20	75
40	63
60	56
80	51
100	43

## CHAPTER IV

## EXPERIMENTS, RESULTS AND DISCUSSION

The experiments were started using the effluent from the Campus oxidation pond. However in the early months of the investigation, the sump well no. 6 pump broke down and the pond did not receive raw sewage leading to a slow death of algae in the pond. This necessitated a set up of algal culture behind the laboratory which has already been described in earlier chapter. These variations of the source of effluents naturally gave varied initial concentrations of algae with a minimum of 88 mg/l and a maximum of 280 mg/l. The species of algae were not very different in the oxidation pond effluents and the laboratory culture since the inoculum for the later was from the former.

The experimental results are classified under two phases.

Concentrating algae under different:

- (i) Physical environmental conditions
- (ii) Chemical environmental conditions

#### 4.1 CONCENTRATING ALGAE UNDER VARIOUS PHYSICAL ENVIRONMENTAL CONDITIONS

A preliminary study to evaluate the effect of varying some physical conditions of the algal environment were tried to get general information on the behaviour of algae. In these experiments algal suspensions were allowed to stand

(1) exposed to light, (2) in darkness at room temperature ( $28^{\circ}\text{C}$  -  $39^{\circ}\text{C}$ ), (3) in darkness at  $4^{\circ}\text{C}$  under laboratory conditions in the deep freeze, (4) at different initial pH conditions adjusted by using concentrated hydrochloric acid and 0.2M sodium hydroxide. The results are presented in Table 4.

There was no significant effect on algal removals in presence or absence of light or under cold conditions. However the removal of algae under different pH conditions is interesting. The colour of algae changed from green to yellow when the pH was 3 and below. Even though the supernatant was clear, indicating removal of algae, there was no significant accumulation of algal mass at the bottom of the container. With higher pH conditions of 11 and above, there was maximum sedimentation at the bottom. Within 30 minutes, there was more than 60 per cent removal under 12 to 12.5 initial pH conditions. Whether it is due to sodium ions ( $\text{Na}^{+}$ ) or hydroxyl ions ( $\text{OH}^{-}$ ), there seems to be certain amount of destabilization of algal cells resulting in concentration of algae in the bottom sediment.

Golueke and Oswald (23) observed that pure culture of chlorella and scenedesmus washed a number of times and suspended in distilled water showed maximum sedimentation at pH 3. Addition of cations like sodium ( $\text{Na}^{+}$ ), Calcium ( $\text{Ca}^{++}$ ), and magnesium ( $\text{Mg}^{++}$ ) up to a concentration of 4 mM did not increase or decrease the flocculation of algae. Observations presented here, are slightly at variance with their results.



TABLE 4

Effect of Physical Environments on Algal Removal

φ

Time in hours	Light (4 Tube- lights 190 ft. candles)- per cent removal	Darkness at (28°C - 34°C)- per cent removal	Cold temperature at 4°C-per cent removal
0	0	0	0
12	11	12	10
24	21	30	14
36	30	35	26
48	35	50	30

φ Initial concentration of algae 164 mg/l, pH 9.5.

While low pH values gave a clearer supernatant, the maximum removal in the acidic range was not at pH 3, perhaps the use of pure cultures and distilled water in the above cited work may be some of the reasons for this. More over it has been also reported by the same authors that chlorella when resuspended in the original culture fluid did not flocculate at pH 3. The cultures used in the present experiments were predominant in chlorella species. The behaviour of the algae in the acidic range is almost similar, to the observation made by Golueke and Oswald (23) as indicated in the Fig. 5 excepting the peak at pH 3.

Change of pH between 5 and 10 has practically no effect on settlement of algae. Increasing removals were observed under the pH conditions of 10.5 to 12.5. Unlike in the acidic range, there is no change of green colour in this range. Even though the volume of sediment was not measured, there was increasing accumulation of algae in the bottom layers of the container. In contrast to the observations in the acidic range algal sedimentation seems to be rapid under alkaline conditions. (Compare the graphs for  $\frac{1}{2}$  hour and 24 hours in the Fig. 5). Irrespective of the theoretical implications in explaining the destabilization of algal cells there is a definite evidence that sedimentation or flocculation is taking place under these conditions. Perhaps magnesium ions are causing destabilization and flocculation as explained by Folkman Yair et al (51). Even though 60 per cent removal of algae in  $\frac{1}{2}$  hour at pH 12, is attractive the economics as

TABLE 5

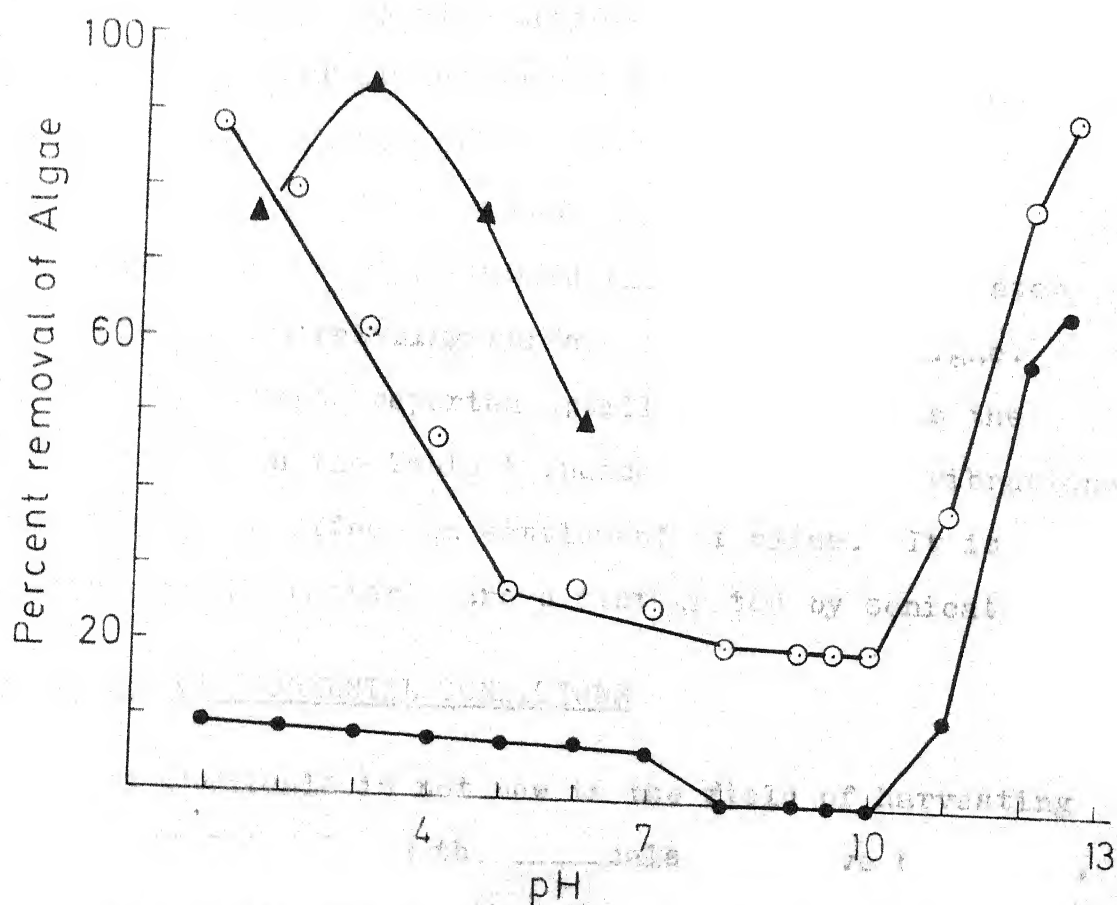
Effect of pH on Algal Removal

Initial Concentration 164 mg/l

Initial pH	1	2	3	4	5	6	7	8	9	9.5	10	11	12	12.5
Final pH after 24 hours	1	1.8	2.5	3.4	4.6	5.7	6.5	7.7	8.8	9.5	9.6	10.4	11.2	11.7
Per cent removal in $\frac{1}{2}$ hour	9.5	9	8.5	8.0	7.4	7.4	5.0	0.0	0.0	0.0	0.0	12.0	60.0	67.0
Per cent removal in 24 hours	88	80	62	48	28	28	26	21	21	21	21	40	80	93
Chemicals used con.														
HCl in ml;	3.2	2.7	2.2	1.7	1.4	1.2	1.0	0.7	0.4	0.0				
0.2N NaOH in ml											5.0	30.0	60.0	110.0

- 1/2 hour setting
- 20 hour
- ▲— Golueke & Oswald (23)

Initial concentration of Algae 164 mg/l  
pH: 9.5



EFFECT OF pH IN CONCENTRATING ALGAE

FIG. 5

well as the need of neutralization at a later time for utilizing the algae make this proposal practically useless.

#### 4.1.1 Ultra Sonic Process

In the recent works on the bioflocculation of micro-organisms (17, 38-40), it was observed that the cells of bacteria and algae extrude an organic polymer that has a capacity to flocculate the microorganisms. Centrifugation at 4000rpm separate the cells from the polymer. It was thought that sonic vibrations may also achieve a similar purpose of separating the polymer or increasing the concentration of polymer by disrupting the cells. Some information was available that algal cells are not easily disrupted by sonicator (52). Golueke and Oswald (23) have used sonicator with the idea of neutralizing surface charge of the algae. But all the experiments reported uptill now as well as the results presented in the Table 6 indicate that sonic vibrations have practically no effect on settlement of algae. It is known, however that bacteria are disintegrated by sonicator.

#### 4.2 CHEMICAL ENVIRONMENTAL CONDITIONS

Use of chemicals is not new in the field of harvesting of algae (23,33,34). Among the chemicals that have been used, the most prominent is alum. Subsequent utilization of concentrated algae as animal feed or for digestion, causes problem because of the high concentration of aluminium ions (17,53). If alum could be replaced by some other chemicals which may be less toxic or if the concentration of alum could

TABLE 6

Effect of Ultra Sonic Vibrations on Algae

	Initial concentration in mg/l	Time of processing in minutes					
		0	6	12	18	24	30
Per cent remaining at 25 mA	95	79	84	87	92	95	100
Per cent remaining at 50 mA	116	80	86	89	93	96	100
Per cent remaining at 75 mA	116	80	85	86	92	97	100
Per cent remaining at 100 mA	130	77	81	86	90	95	100

be reduced by using coagulant aids or other coagulants it may give a more useful algal product that can be put for further use. With this view in mind the following chemicals and natural polyelectrolytes described elsewhere have been used, singly and in combination. It is observed in many of the experiments that longer settling time of 20 hours did not appreciably increase the algal concentration over and above the  $\frac{1}{2}$  hour settling time. Even though observations on 20 hours of settling in all experiments are presented, only the results with  $\frac{1}{2}$  hour settling are taken as significant from practical consideration. The results using single chemicals are presented in the following pages.

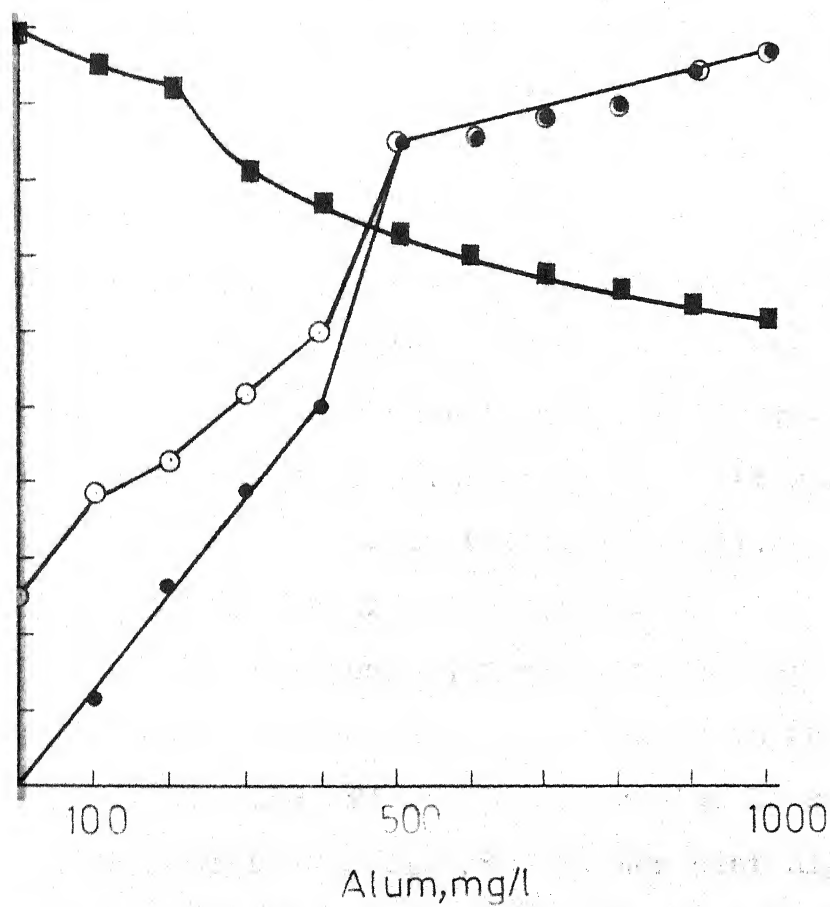
#### 4.2.1 Effect of Alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ] in Concentrating Algae

The experiments using alum and filter alum (a sample obtained through the courtesy of Kanpur Water Works) are used in these experiments. pH was not controlled in any of these experiments, but was measured and reported in all experiments.

The effect of alum on the concentrating algae in  $\frac{1}{2}$  hour and 20 hours is presented in Fig. 6. The removal of algae in  $\frac{1}{2}$  hour was almost linear up to a dose of 400 mg/l, with a 50 per cent removal at pH 7.7. There is a steep increase after this point when the removal become 85 per cent with an increased dose of 100 mg/l more resulting in a decrease of pH to 7.3. No significant removal concurrent with increase in alum dose was observed after this dose of 500 mg/l. Even though pH decreased to 6.8 at 700 mg/l of alum there is not

- pH
- 1/2 hour settling
- 20 hours "

Initial concentration of Algae : 244 mg/l



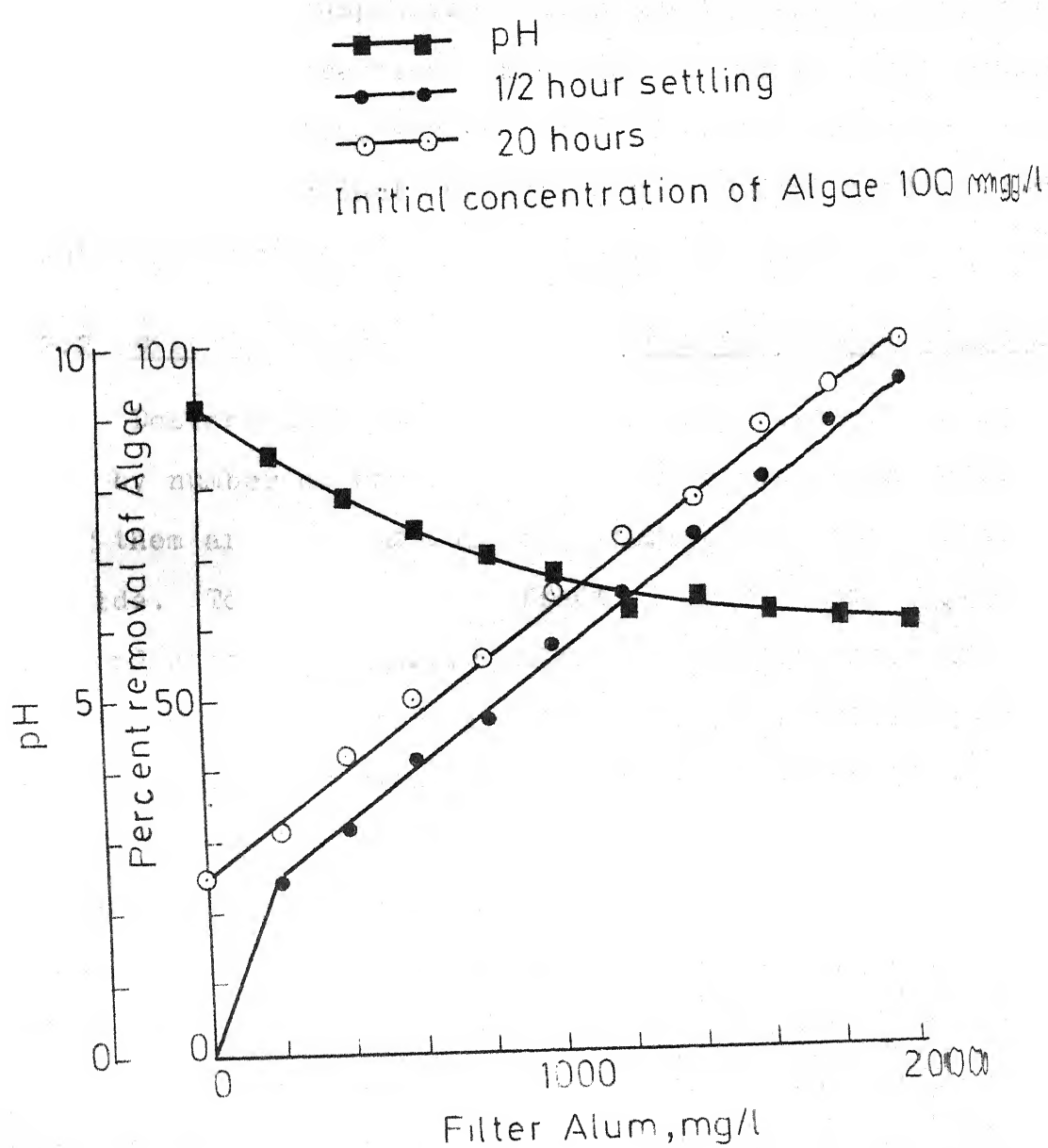
EFFECT OF ALUM IN CONCENTRATING ALGAE

FIG. 6



much of additional removal. The maximum removal with the maximum dose of 1000 mg/l of alum was only 13 per cent more than that obtained at half of this dose. The pH was depressed to 6.2 at the maximum dose. According to Sinha (26) the maximum removal of algae with a dose of 400 mg/l was 89 at pH 7. While without pH adjustment the dose required for similar removal was 1000 mg/l. With a high initial concentration of 525 mg/l of algae Saini (21) found that pH adjustment from 8.9 to 7.0 reduced the dose requirement from 2000 mg/l to 1000 mg/l of alum. However in the work of Golueke and Oswald (23) it was mentioned that "best removal of algae was obtained with a pH 6.5 of the suspension; a slightly less removal was obtained when it approached to 6 or 6.8". Since the objective in these experiments was only to find out the effect of alum alone on concentrating the algae and pH adjustment needs another chemical, i.e. acid, those experiments with pH adjustments are described and discussed later. Alum itself being acidic salt brings down the pH and perhaps this results in better removals.

The filter alum is reported to have 14 per cent of  $\text{Al}_2\text{O}_3$  which is almost equivalent to 22 per cent of  $(\text{Al}_2\text{SO}_4)$  alum. Based on the results presented in the Fig. 7 it can be said that the effect of filter alum is similar to that of alum reported earlier. For 85 per cent algal removal there is a requirement of high dose of filter alum of 1400 mg/l which corresponds to about 308 mg/l as  $(\text{Al}_2\text{SO}_4)$  aluminium sulphate. However the steep increase in the removal was



EFFECT OF FILTER ALUM IN CONCENTRATING ALGAE

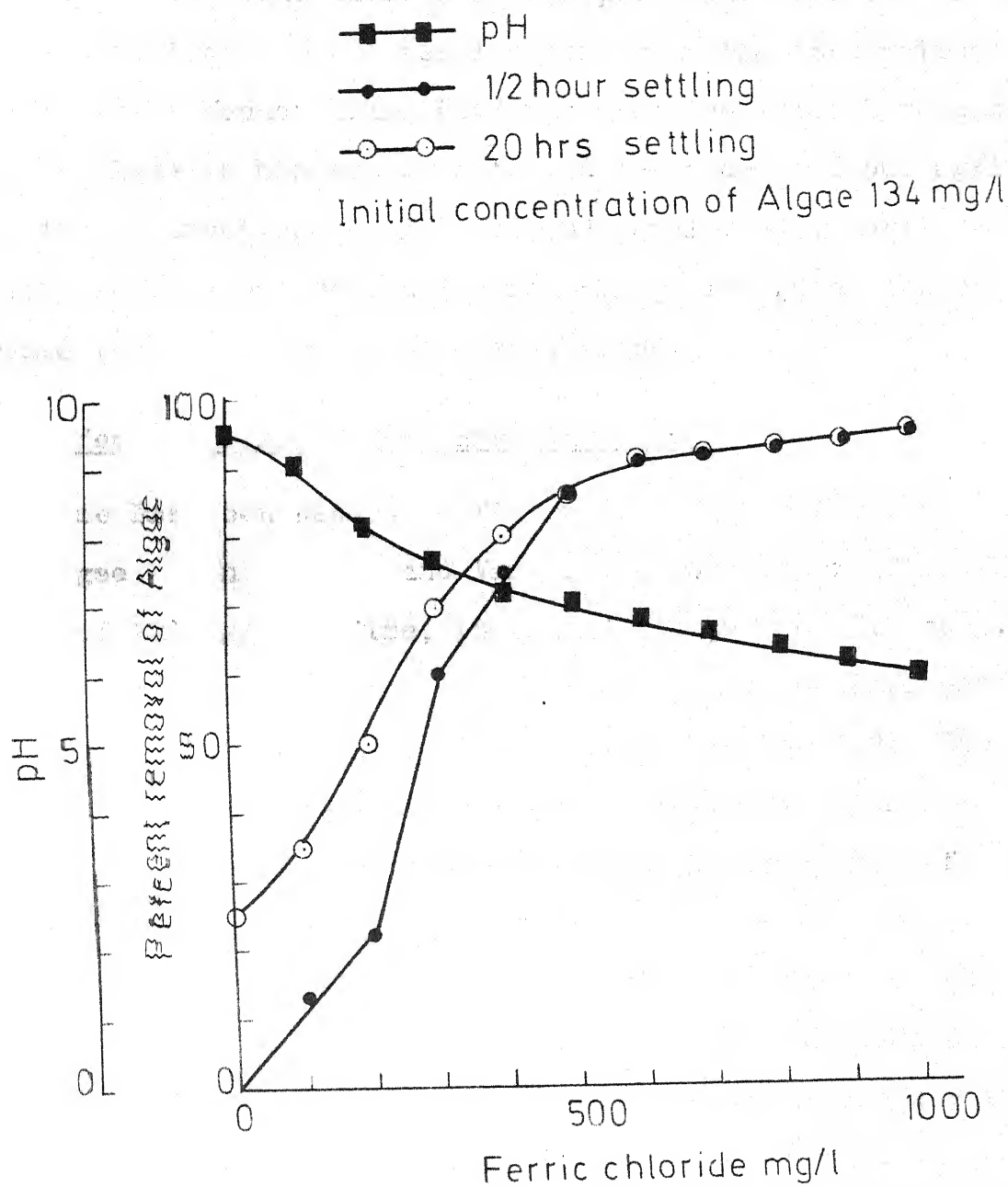
FIG. 7

observed between doses of 12000 mg/l and 1400 mg/l. The pH change was nominal from 6.4 to 6.3. The low dose requirement as aluminium sulphate is due to the low initial concentration of algae in the suspension. Even though filter alum is less expensive than pure alum the need of using higher concentrations may preclude any economic advantage obtained in using the commercial product, excepting the availability in large quantities in market.

#### 4.2.2 Effect of Ferric Chloride Alone in Concentrating Algae

Destabilization of colloidal particles are brought about by number of chemicals other than aluminium salts. Among them are ferrous sulphate, ferric sulphate and ferric chloride. To find out the effect of ferric ions experiment was conducted using ferric chloride. Ferrous sulphate did not give any significant removal of algae which also could not be measured quantitatively because of the yellow colour imparted to the suspension uniformly. Golueke and Oswald (23) had used ferrous sulphate in combination with lime. The use of ferric hydroxide imparted an orange colour to the sludge of the algae. In the experiments using ferric chloride it was found that the yellowish colour of the suspension settled down along with algal cells leaving clear supernatant. The results are presented in Fig. 8.

With 200 mg/l of ferric chloride the removal of algae was merely 22 per cent with a pH reduction upto 8.2. By the addition of another 100 mg/l of ferric chloride (total 300 mg/l)



EFFECT OF FERRIC CHLORIDE IN CONCENTRATING ALGAE

FIG. 8

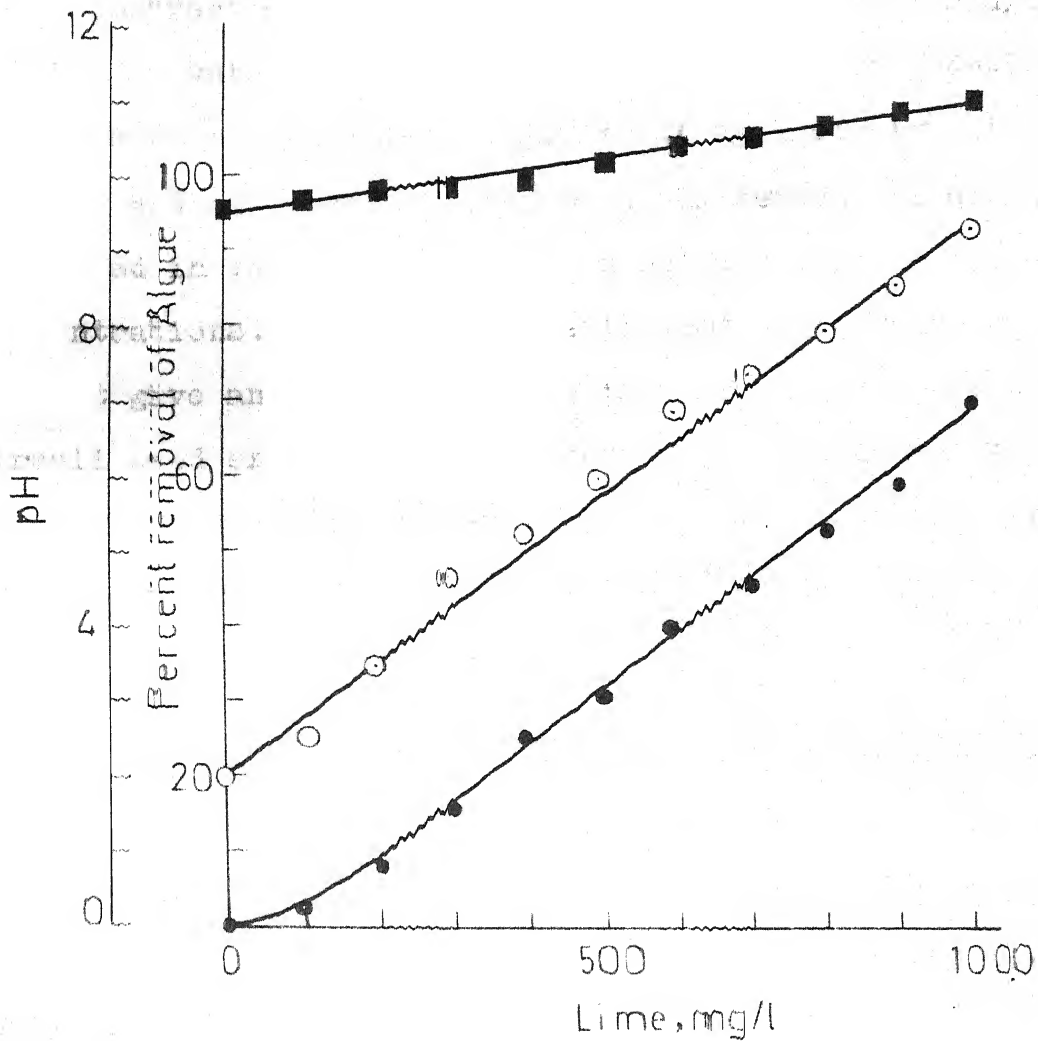
it was observed a settlement of 60 per cent and a pH of 7.6. Further additions gave maximum of 85 per cent removal when 500 mg/l of ferric chloride was added. Beyond this concentration of the chemical there was no appreciable increase in the algal flocculation. These results confirmed the observations made earlier by Madhav Tikhe (54) who used low initial concentration of algae in his experiments. After a dose of 500 mg/l, unlike the observations of Golueke and Oswald (23), ferric chloride algal precipitation did not change its green colour to orange within 20 hours of observations.

#### 4.2.3 Effect of Lime in Concentrating Algae

Lime has been used as a flocculant by some workers to remove algae. Van Vauuren and Van Durren (32) reported that addition of 220 mg/l of lime, increased the pH from 7.7 to 9.7 removing 53 per cent of algae while addition of 600 mg/l gave 71 per cent removal of algae increasing the pH to 11.2. The work of Folkman Yair et al (51) suggests that Magnesium hydroxide particulates are responsible for flocculation of algae, whereas the calcium ions seem to be ineffective. Golueke and Oswald (23) used lime primarily to raise the pH from 9.6 to 11.1. It is stated that up to a pH increase of 10.5 very little precipitation occurred but when increased to 10.6, it resulted in the removal of most of the algae. The experimental results of the present work are plotted in Fig. 9. These do not agree with the observations of Golueke and Oswald (23) but more in confirmity with the results presented by the

- pH
- 1/2 hour settling
- 20 hour

Initial concentration of Algae 174mg/l



EFFECT OF LIME IN CONCENTRATING ALGAE

FIG. 9

workers indicated in the reference (32). The maximum pH of 11.0 was obtained with the use of 1000 mg/l of lime with  $\frac{1}{2}$  hour detention time, the removal of algae being 70 per cent and in 20 hours this increased to 90 per cent. The removals between two settlement times were almost uniform.

#### 4.2.4 Effect of Nirmali Seed Extract in Concentrating Algae

Extract of nirmali seed has been used as a coagulant aid in the water treatment by number of workers (44-47). In concentrations varying from 0.2 to 40 mg/l of nirmali seed extract did not show any effect on the removal of algae as indicated in Table 7. The pH was not affected in any of the concentrations. The time of settlement up to 20 hours, also did not give any removal. From this result it is clear that nirmali seed extract cannot function as a coagulant by itself in harvesting algae. However there is some evidence that it may work as a coagulant in inorganic turbidity removal when the turbidity is more than 300 mg/l.

#### 4.2.5 Effect of Crotalaria Seed Extract in Concentrating Algae

The crotalaria seed extract has not been used till now as a coagulant or as a coagulant aid as described earlier.

The crotalaria seed extract seems to behave as a anionic polyelectrolyte on inorganic turbidity. When used in concentrating algae, with the doses ranging from 0 to 100 mg/l with 20 hours settling, there was no significant removal of algae. The results are tabulated in Table 8. The experiments on the removal of inorganic turbidity presented in the earlier chapter

TABLE 7

Effect of Nirmali seed extract in concentrating algae

Initial Concentration of Algae 122 mg/l

Settling time 20 hours

Dose of nirmali seed extract in mg/l	Per cent removal of algae
0.0	29
0.2	25
0.4	25
0.6	25
0.8	25
1.0	29
2.0	25
4.0	25
6.0	22
8.0	22
10.0	29
20.0	24
40.0	24
60.0	24
80.0	24
100.0	24



gives an interesting observation that this natural anionic polyelectrolyte is able to act on inorganic turbidity and fails with organic colloids.

TABLE 8

Initial Concentration of Algae 128 mg/l

pH 9.8

Settling time 20 hours.

Dose of crotalaria seed extract in mg/l	0	20	40	60	80	100
Per cent removal	32	47	55	46	45	41

#### 4.2.6 Effect of Combinations of Chemicals in Concentrating Algae

In the process of concentrating solids from liquid—solid stable suspensions, one can distinguish two different phenomenon that are essential for successful separation. The naturally similarly charged particles must be made to come and stick together and later flocculate to form a concentrated sludge. Alum is one of the chemicals that normally brings about this change by neutralizing the charge and the metal hydroxide entraps and adsorbs the particles, and settles down as sediment. Similar action is also shown by ferric salts. The process of destabilization seems to be the first step necessary for successful separation of solids, by providing other chemical species that can help in destabilization of the particle and it may decrease the concentration of the primary coagulant dose to a non toxic level in the sludge. The other phenomenon of

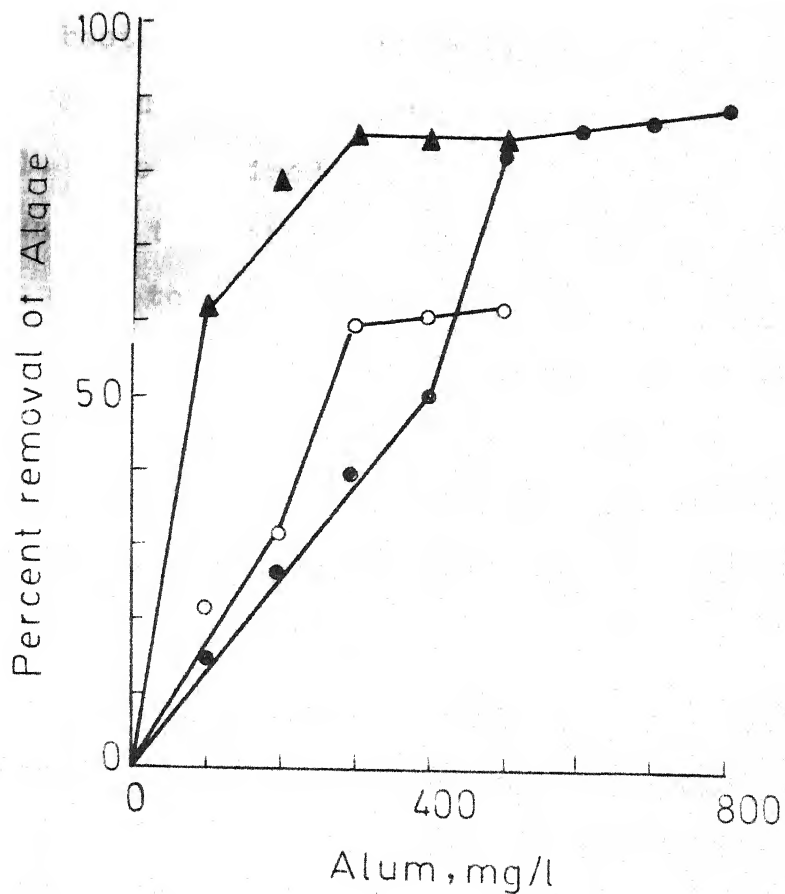
CENTRAL

the coagulant aids is called the bridging effect, that is evident only in the presence of calcium and magnesium ions. The bridging will effectively help in reducing the amount of coagulant required for flocculation. The chemicals that have been used in combination can be considered as those helping the destabilization process and further in the flocculation process or in both.

#### 4.2.6.1 Combined Effect of Alum and Acid in Concentrating Algae:

Even though acid is used mainly to bring down the pH, it is also used as a chemical in addition to the alum. The experimental results are discussed in this section. From the literature cited earlier alum is known to function better under near reduced pH conditions. In the report of Golueke and Oswald (23) it has been mentioned that pH of 6.5 was best suited for removal of algae and less removal was obtained when it is reduced or increased. Saini (21) as well as Sinha (26) found the best removals under pH 7. Since the object is to reduce alum dosage, the pH of algal suspension was reduced from 9.6 to 7 and 6 with concentrated sulfuric acid before the addition of different concentrations of alum. The Fig. 10 indicates, 85 per cent of algal removal could be obtained when the pH was adjusted to 6, and with 300 mg/l of alum while this much of concentration of algae could be obtained with 500 mg/l of alum alone, when the final pH without adjusting was found to be 7.3. There was a definite increase in settling of algae even when the pH was adjusted to 7. It is already seen that simple adjustment of pH alone in the acidic range was not effective.

iformly, which must have given a  
 float. Similar observations  
 thought that the  
 Initial concentration of Algae 164 mg/l



COMBINED EFFECT OF ACID AND ALUM IN  
 REMOVAL OF ALGAE

An interesting observation is that when concentrated sulphuric acid was used for pH adjustment the settled algal sludge as a body floated up to the surface like bulking sludge. By close observations it was observed that tiny gas bubbles were entrapped in the floc uniformly, which must have given buoyancy for the algal sludge to float. Similar observation was also made by Parker (55) who thought that the sludge floated because of photosynthetic organisms.

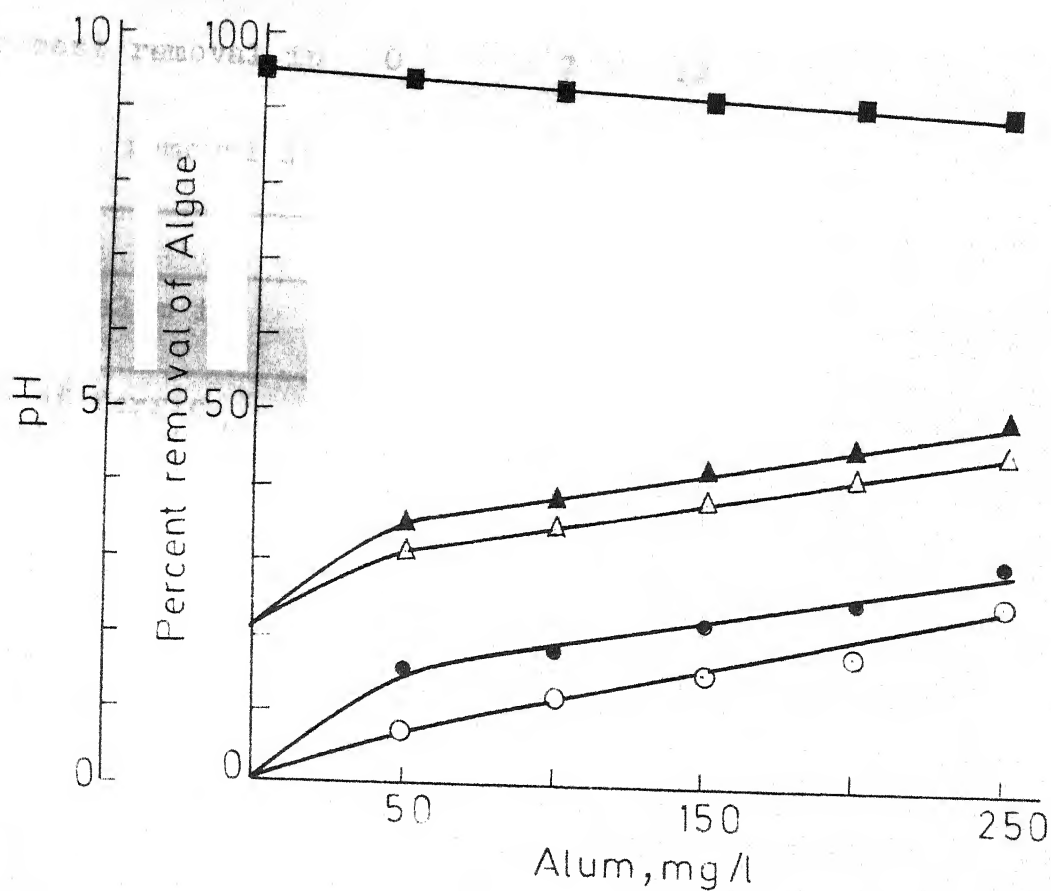
#### 4.2.6.2 Combined Effect of Alum and Ferric Chloride in Concentrating Algae:

While the best removals was obtained with 500 mg/l alum alone, 500 mg/l ferric chloride alone was also required for the same removal. The combined effect of chemicals is shown in the Fig. 11 and in the Table 9. The combination of these chemicals do not seem to improve or add effectively to the removals of algae. 250 mg/l of alum alone in  $\frac{1}{2}$  hour removed 33 per cent while in combination with 40 mg/l of ferric chloride which was found to be optimum, the removals were only 30 per cent. So the combination of these two chemicals is not indicative for practical purposes.

#### 4.2.6.3 Combined Effect of Lime and Alum in Concentrating Algae:

The combination of lime and alum however showed more promise when compared to alum and ferric chloride combination. The results are presented in the Fig. 12 and 13. While 250 mg/l of lime alone gave a 13 per cent concentration of algae, 100 mg/l of alum alone gave 16 per cent removal of algae. Both the chemicals together in the same concentrations, viz., lime

■—■ pH  
 ●—● 40 mg/l to 100 mg/l Ferric chloride } 1/2 hr settling  
 ○—○ 20 mg/l Ferric chloride }  
 ▲—▲ 40 to 100 mg/l Ferric chloride } 20hrs settling  
 △—△ 20 mg/l Ferric chloride }  
 Initial concentration of Algae 164 mg/l



COMBINED EFFECT OF ALUM AND FERRIC CHLORIDE IN CONCENTRATING ALGAE

FIG. 11

TABLE 9

Combined Effect of Alum and Ferric Chloride  
in Concentrating Algae

Initial Concentration of Algae 164 mg/l

Dose of alum in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	20	20	20	20	20
pH	9.4	9.3	9.2	9.1	9.0	8.9
Per cent removal in $\frac{1}{2}$ hour	0	7	12	15	18	25
Per cent removal in 20 hours	21	32	35	39	43	45

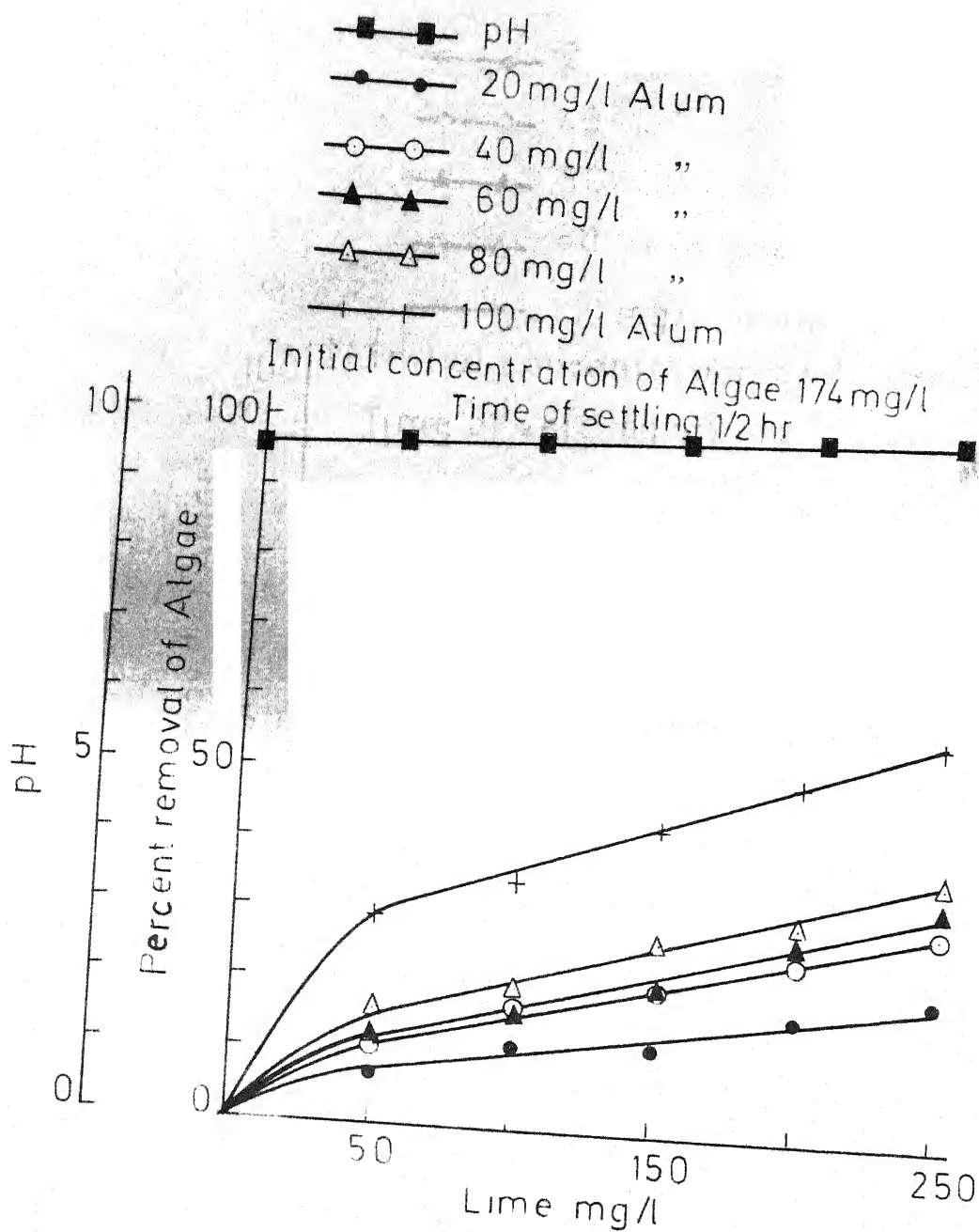
Dose of alum in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	40	40	40	40	40
pH	9.5	9.4	9.3	9.2	9.1	9.0
Per cent removal in $\frac{1}{2}$ hour	0	15	18	22	25	30
Per cent removal in 20 hours	21	35	39	43	45	50

Dose of alum in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	60	60	60	60	60
pH	9.5	9.4	9.3	9.2	9.1	9.0
Per cent removal in $\frac{1}{2}$ hour	0	15	18	21	28	30
Per cent removal in 20 hours	21	35	43	44	50	52

Table 9 (Continued)

Dose of alum in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	80	80	80	80	80
pH	9.5	9.4	9.2	9.1	9.0	8.9
Per cent removal in $\frac{1}{2}$ hour	0	15	18	22	27	30
Per cent removal in 20 hours	21	35	39	43	45	50

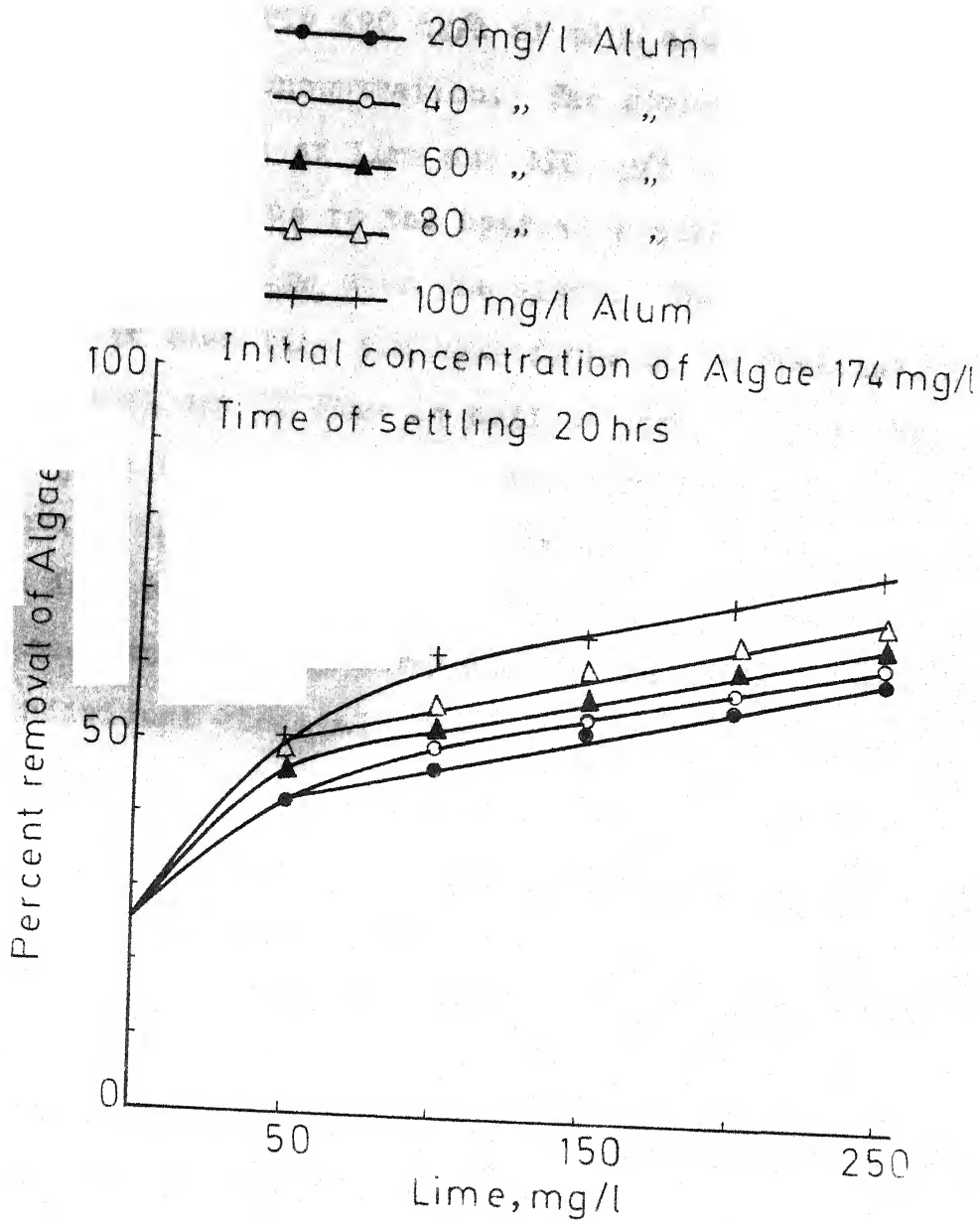
Dose of alum in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	100	100	100	100	100
pH	9.5	9.3	9.2	9.1	9.0	8.9
Per cent removal in $\frac{1}{2}$ hour	0	15	18	22	24	30
Per cent removal in 20 hours	21	35	35	39	43	48



COMBINED EFFECT OF LIME AND ALUM IN CONCENTRATING ALGAE

FIG. 12





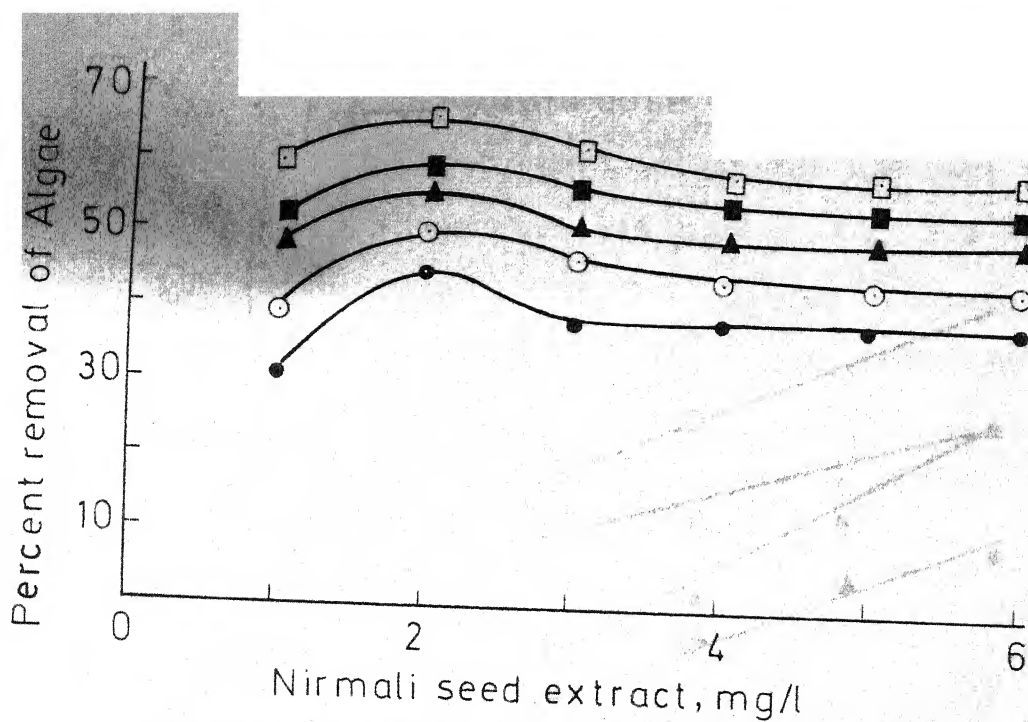
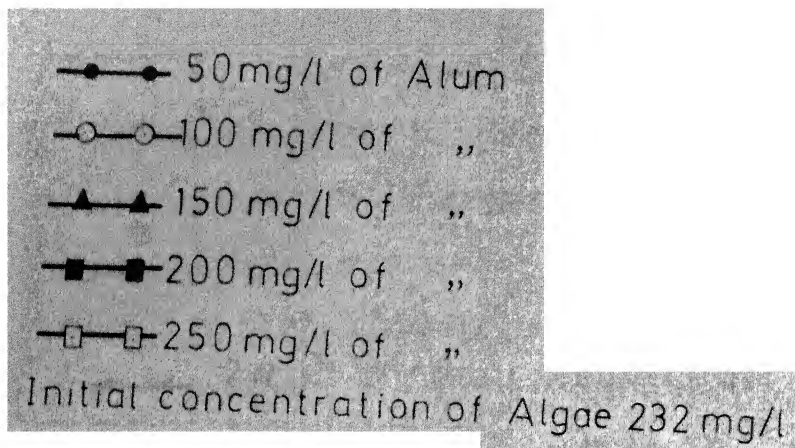
COMBINED EFFECT OF LIME AND ALUM IN  
CONCENTRATING ALGAE

FIG.13

250 mg/l and alum 100 mg/l, gave 55 per cent concentrated algae in  $\frac{1}{2}$  hour. It is interesting to note that to bring about 55 per cent algal concentration, 800 mg/l of lime alone was required. Similarly 420 mg/l of alum alone was required to obtain the same concentration. The combination indicates a saving of 550 mg/l of lime and 320 mg/l of alum. The mechanism most probably is due to the hydroxide alkalinity provided by the lime, in settling down the algae. There was no significant change in pH when lime and alum alone or in combination were used. The amount of alum as well as lime could be brought down to  $\frac{1}{4}$  of their individual concentrations required. It is also interesting to note that combination yields profitable results in  $\frac{1}{2}$  hour settlement. The results of 20 hours settling do not seem to show any advantage in using the combination since individual chemicals are giving  $\frac{1}{2}$  of the total settlement in 20 hours.

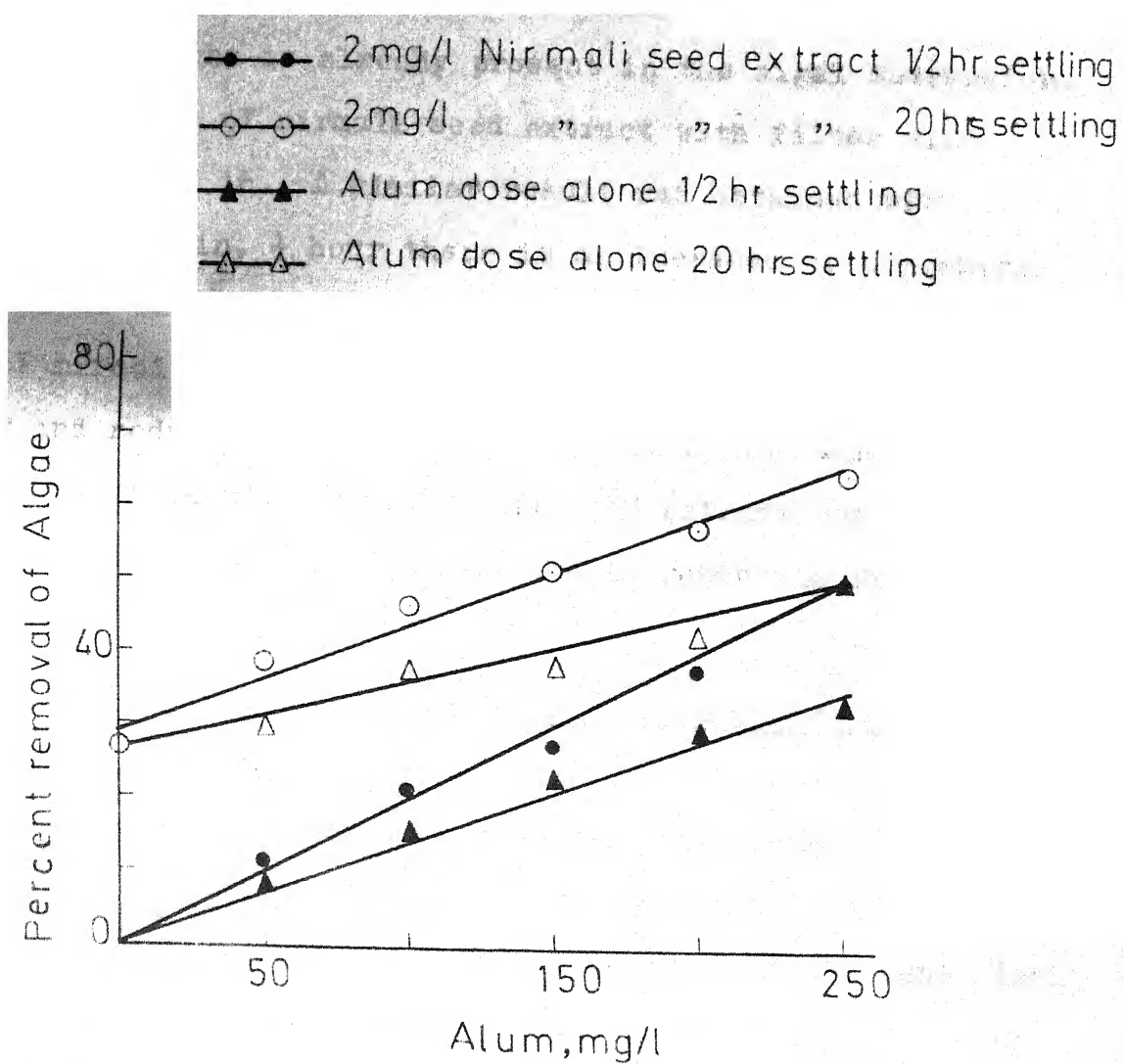
#### 4.2.6.4 Combined Effect of Alum and Nirmali Seed Extract in Concentrating Algae:

The combination of alum and nirmali seed extract were tried since it was known to give good results in water purification. Interesting to note that irrespective of alum dose, the optimum concentration of nirmali seed extract was found to be 2 mg/l. This has been used with various concentrations of alum, and the results are presented in the Fig. 14 and 15. Combination with nirmali seed extract yielded 30 per cent more algal harvesting than alum alone when used in concentration of 250 mg/l in  $\frac{1}{2}$  hour detention time. The same

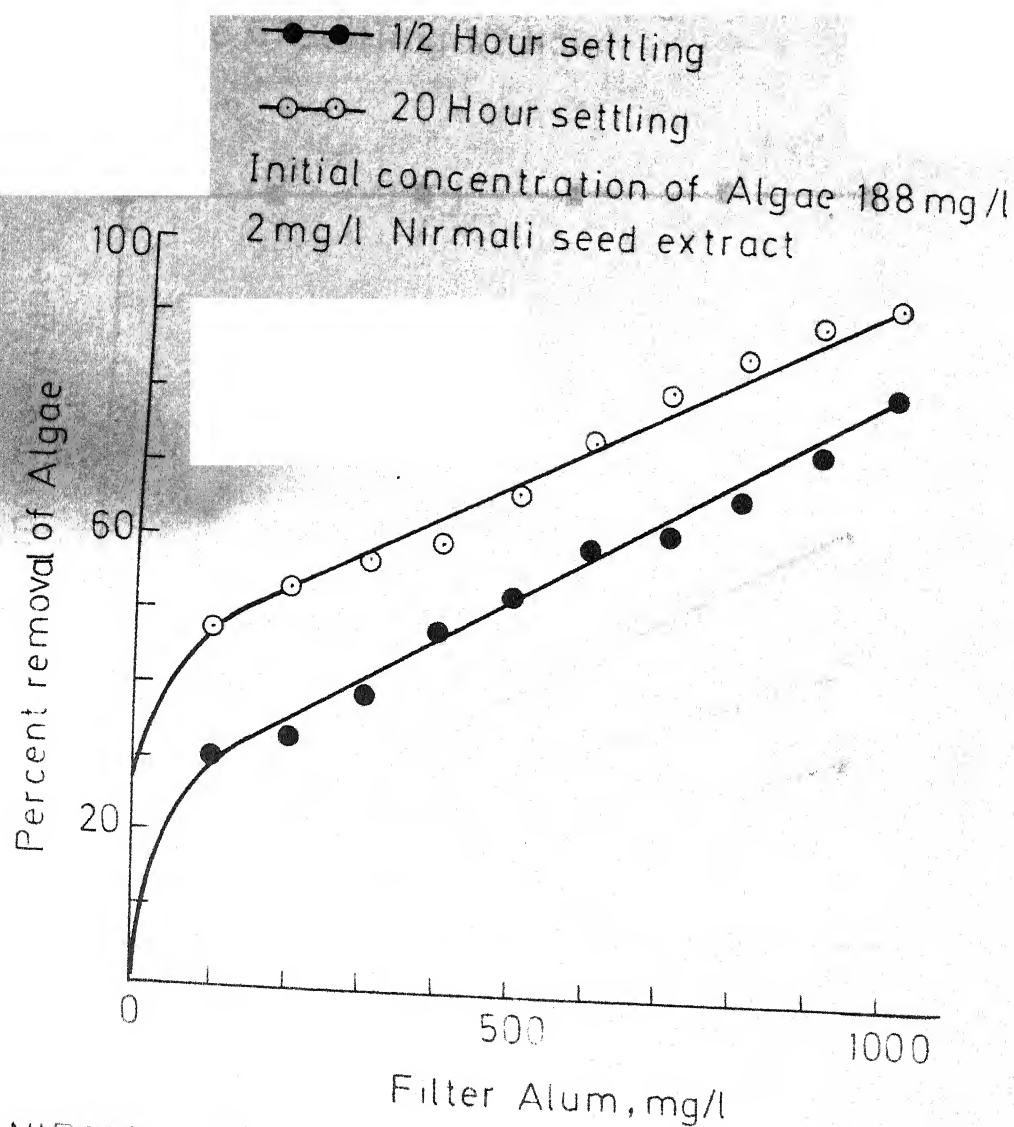


OPTIMUM DOSE OF NIRMALI SEED EXTRACT

FIG.14



NIRMALI SEED EXTRACT AS A COAGULANT AID  
WITH ALUM IN REMOVAL OF ALGAE

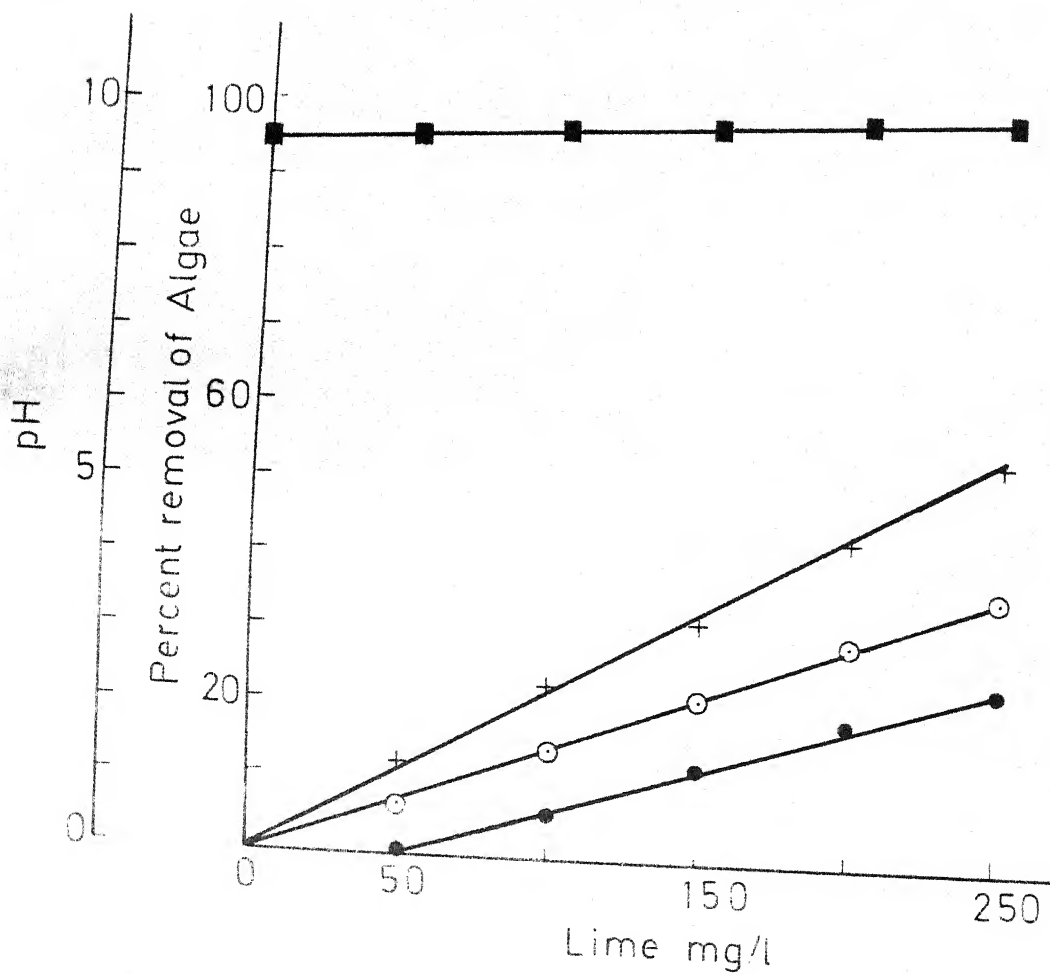


NIRMALI SEED EXTRACT AS A COAGULANT AID WITH  
FILTER ALUM IN REMOVAL OF ALGAE

FIG.16

- — ■ pH
- + — + 60 mg/l, 80 mg/l, 100 mg/l Ferric chloride
- — ○ 40 mg/l Ferric chloride
- — ● 20 mg/l Ferric chloride

Initial concentration of Algae 164 mg/l  
Time of settling 1/2 hour

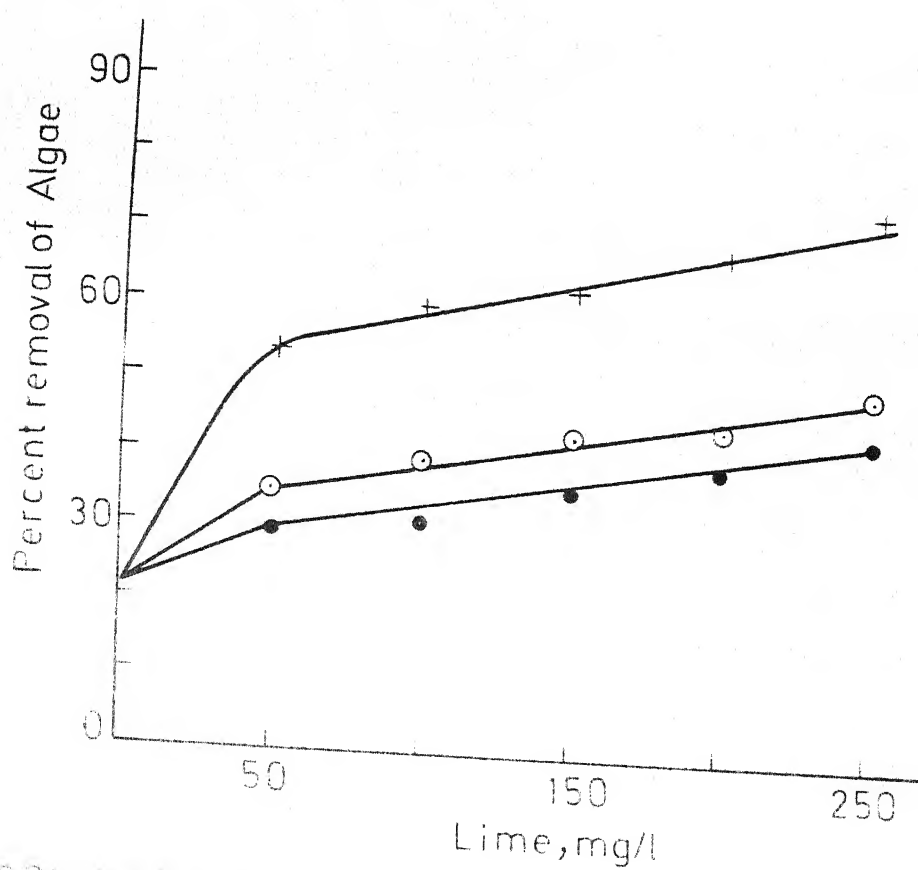


COMBINED EFFECT OF LIME AND FERRIC CHLORIDE IN  
CONCENTRATING ALGAE

FIG.17

—+—+—+ 60 mg/l , 80 mg/l , 100mg/l , Ferric chloride  
—○—○—○ 40 mg/l Ferric chloride  
—●—●—● 20 mg/l Ferric chloride

Initial concentration of Algae 164 mg/l  
Time of settling 20 hours



COMBINED EFFECT OF LIME AND FERRIC CHLORIDE  
IN CONCENTRATING ALGAE

FIG.18

of lime or 280 mg/l of ferric chloride. By the method of this combination the concentration of these chemicals was significantly brought down, when  $\frac{1}{3}$  of the lime and  $\frac{1}{5}$  of the ferric chloride were used. There was no significant change in pH. The mechanism seems to be simple formation of hydroxide of iron. There was no colour change in the supernatant. Similar observations as those of lime and alum combinations were observed in 20 hours settling time. There seems to be no advantage obtained by increasing the sedimentation time. Moreover it seems to offset any advantage gained by the combinations of chemicals since the total sedimentation of individual chemicals was almost the same level as that of combination. This is a point of advantage in designing flocculation and sedimentation tank where shorter detention times are desirable. Experimental results are tabulated in Table 10.

#### 6.6 Combined Effect of Nirmali Seed Extract and Ferric Chloride in Concentrating Algae:

The results of mixing nirmali seed extract and ferric chloride were disappointing as it can be seen from the Fig. 19 Table 11. The seed extract antagonistically reduces the coagulation of algae from 85 per cent to 42 per cent in  $\frac{1}{2}$  hour and from 85 per cent to 50 per cent in 20 hours. It seems as though nirmali seed extract protects the algae from being coagulated and flocculated by ferric chloride.

#### 6.7 Combined Effect of Nirmali Seed Extract and Lime in Concentrating Algae:

Marginal advantage was noticed when lime and nirmali



TABLE 10

Combined Effect of Lime and Ferric Chloride  
in Concentrating Algae

Initial Concentration of Algae 164 mg/l

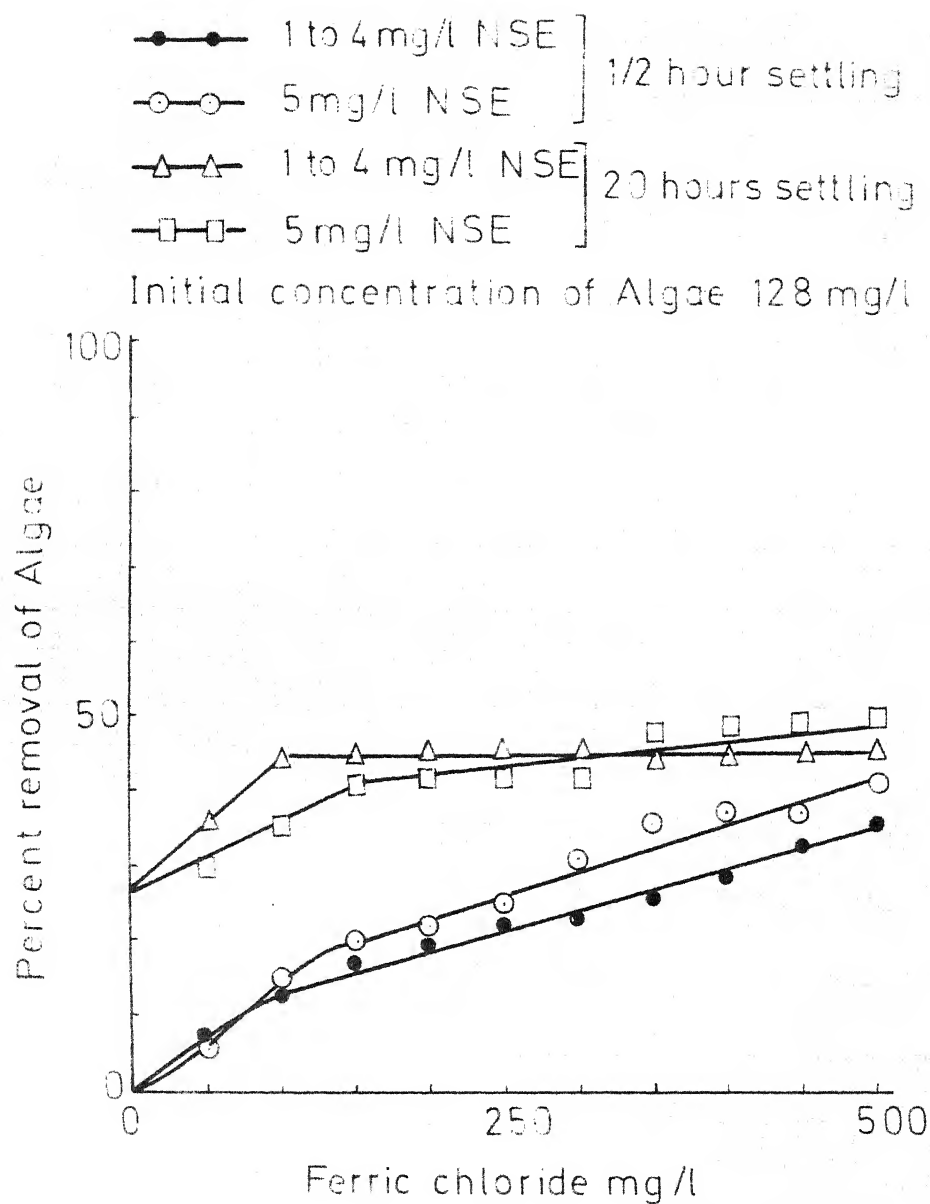
ose of lime in g/l	0	50	100	150	200	250
se of ferric loride in mg/l	0	20	20	20	20	20
	9.5	9.6	9.6	9.8	9.9	10.0
r cent removal in hour	0	0	3.5	7	12	15
r cent removal in hours	21	30	31	36	39	44
e of lime in l	0	50	100	150	200	250
e of ferric oride in mg/l	0	40	40	40	40	40
	9.5	9.6	9.7	9.8	9.9	10.0
cent removal in our	0	7	15	22	30	36
cent removal in ours	21	35	39	43	45	50

Table 10 (Continued)

Dose of lime in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	60	60	60	60	60
pH	9.5	9.7	9.8	9.9	10.0	10.0
Per cent removal in $\frac{1}{2}$ hour	0	15	25	32	42	54
Per cent removal in 20 hours	21	54	62	63	68	74

Dose of lime in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	80	80	80	80	80
pH	9.5	9.7	9.8	9.9	10.0	10.0
Per cent removal in $\frac{1}{2}$ hour	0	15	22	36	43	54
Per cent removal in 20 hours	21	54	63	63	68	74

Dose of lime in mg/l	0	50	100	150	200	250
Dose of ferric chloride in mg/l	0	100	100	100	100	100
pH	9.5	9.7	9.8	9.8	9.9	10.0
Per cent removal in $\frac{1}{2}$ hour	0	15	22	36	39	50
Per cent removal in 20 hours	21	54	68	72	74	78



EFFECT OF NIRMALI SEED AS A COAGULANT AID  
WITH FERRIC CHLORIDE IN CONCENTRATING ALGAE

FIG. 19

TABLE 11

Combined Effect of Nirmali Seed Extract and  
Ferric Chloride in Concentrating Algae

Initial Concentration of Algae 128 mg/l

Dose of ferric chloride in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	1	1	1	1	1
pH	9.7	9.5	8.6	7.8	7.6	7.3
Per cent removal in $\frac{1}{2}$ hour	0	13	20	22	26	36
Per cent removal in 20 hours	27	45	45	45	45	45

Dose of ferric chloride in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	2	2	2	2	2
pH	9.7	8.9	8.7	7.7	7.5	7.3
Per cent removal in $\frac{1}{2}$ hour	0	13	20	22	26	36
Per cent removal in 20 hours	27	41	45	45	45	45

Dose of ferric chloride in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	3	3	3	3	3
pH	9.7	9.4	8.6	8.2	7.5	7.3
Per cent removal in $\frac{1}{2}$ hour	0	18	26	32	32	36
Per cent removal in 20 hours	27	41	45	45	45	45

Table 11 (Continued)

Dose of ferric chloride in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	4	4	4	4	4
pH	9.7	9.0	8.8	8.3	7.7	7.4
Per cent removal in $\frac{1}{2}$ hour	0	13	22	32	32	32
Per cent removal in 20 hours	27	36	41	45	45	45

## Initial Concentration of Algae 100 mg/l

Dose of ferric chloride in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	5	5	5	5	5
pH	9.7	9.0	8.8	8.3	7.6	7.3
Per cent removal in $\frac{1}{2}$ hour	0	12	22	30	36	41
Per cent removal in 20 hours	27	30	41	41	47	47

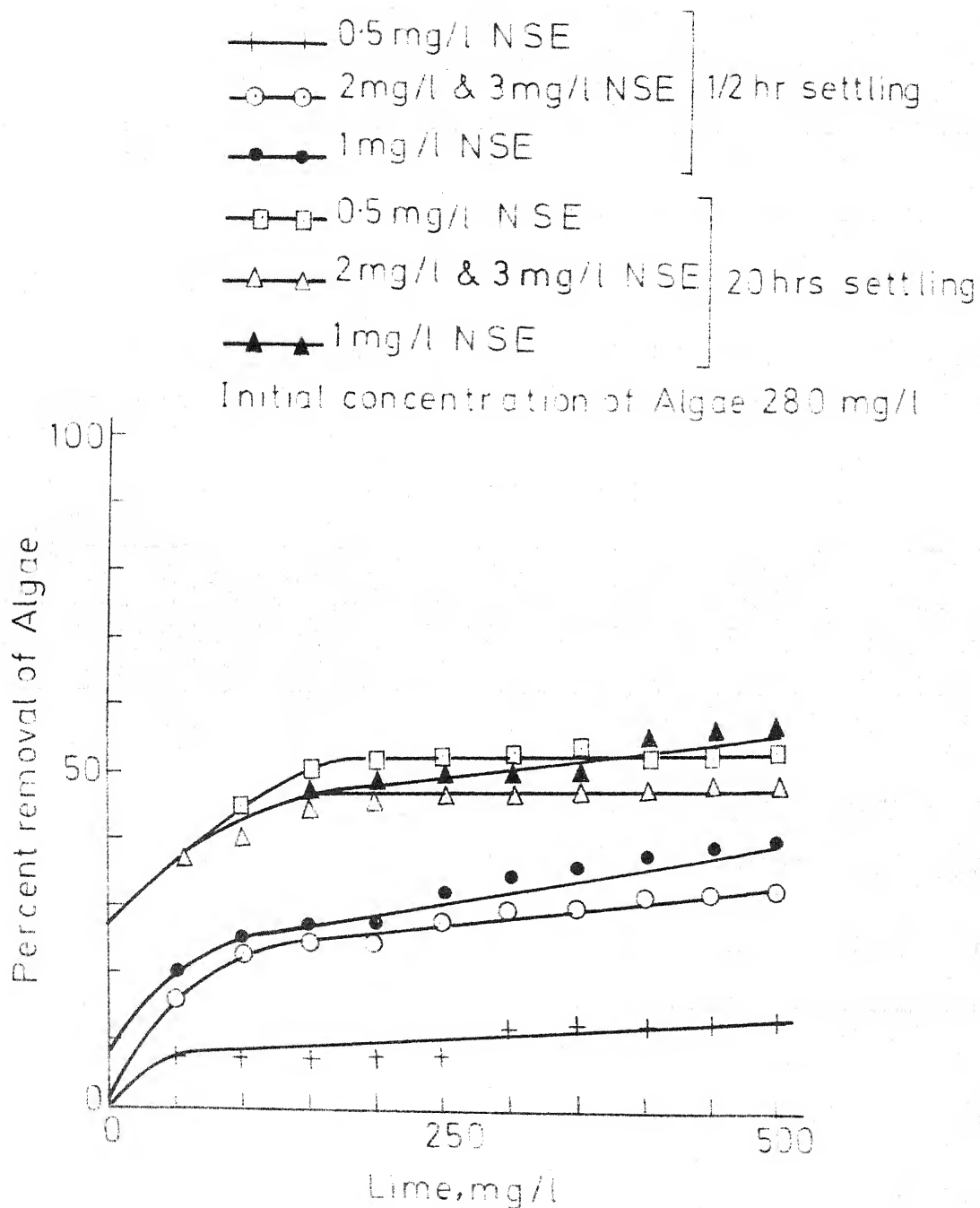
seed extract were used. The result is presented in the Fig. 20 and in the Table 12. Only 9 per cent removal of algae more than the control was observed in  $\frac{1}{2}$  hour settling and negative result in 20 hours. It is clear that even though calcium is expected to provide necessary condition for bridging in presence of coagulants like alum, which by itself can not bring about better coagulation in presence of seed extract.

#### 4.3 COST ANALYSIS

Taking the commercial cost of the chemicals used (50) the total cost of producing one Kg dry weight of algae was calculated to obtain the comparative estimates in each of the experiments. This information is summerized in the Table 13. The cost of pure alum is from the chemical catalogue and is included only for information and can not be compared in the real sense with the cost of the other chemicals.

It is clear from the presented data that even though lime by itself was not as efficient as other chemicals used singly, the cost is minimum with lime (Rs 2.90/Kg of dry weight algae). The cost of nirmali seed powder is not available. More over per Kg of harvested algae only 10 gms of nirmali seed is required when used with lime. Among all the combinations this combination seems to be most economical (Rs 1.75/Kg of dry weight algae) even though the per cent removal is only 40 per cent. There is no significant change in the pH in this combination.

Lime and ferric chloride are as good as lime alone in



EFFECT OF NIRMALI SEED AS A COAGULANT AID  
WITH LIME IN CONCENTRATING ALGAE

TABLE 12

Combined Effect of Nirmali Seed Extract  
and Lime in Concentrating Algae

Initial Concentration of Algae 200 mg/l

Dose of lime in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	0.5	0.5	0.5	0.5	0.5
pH	9.1	9.2	9.3	9.3	9.3	9.3
Per cent removal in $\frac{1}{2}$ hour	0	7	7	13	13	13
Per cent removal in 20 hours	30	42	48	48	48	48

Initial Concentration of Algae 280 mg/l

Dose of lime in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	1	1	1	1	1
pH	9.1	9.1	9.2	9.2	9.3	9.3
Per cent removal in $\frac{1}{2}$ hour	0	25	28	33	38	44
Per cent removal in 20 hours	30	46	50	50	54	54



Table 12 (Continued)

Initial Concentration of Algae 266 mg/l

Dose of lime in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	2	2	2	2	2
pH	9.1	9.1	9.2	9.2	9.2	9.3
Per cent removal in $\frac{1}{2}$ hour	0	25	25	30	32	32
Per cent removal in 20 hours	30	35	47	47	52	56

Initial Concentration of Algae 266 mg/l

Dose of lime in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	3	3	3	3	3
pH	9.1	9.2	9.2	9.3	9.3	9.3
Per cent removal in $\frac{1}{2}$ hour	0	24	32	32	32	32
Per cent removal in 20 hours	30	42	47	47	47	47

Initial Concentration of Algae 232 mg/l

Dose of lime in mg/l	0	100	200	300	400	500
Dose of nirmali seed extract in mg/l	0	4	4	4	4	4
pH	9.1	9.1	9.2	9.3	9.3	9.3
Per cent removal in $\frac{1}{2}$ hour	0	20	25	25	30	30
Per cent removal in 20 hours	30	45	50	50	50	50

TABLE 13

## Cost Analysis

Cost of chemicals in Rs.:

(1) Pure alum	36.50/Kg
(2) Filter alum (21 per cent pure alum)	0.65/Kg
(3) Ferric chloride	2.00/Kg
(4) Lime	0.35/Kg
(5) Sulphuric acid (Naked)	0.40/Kg

Chemicals used	Quantity of chemicals in Kg	Cost in Rs./Kg of harvested algae (dry weight)
Pure alum	2.5	89.00
Filter alum	11.0	7.15
Lime	8.3	2.90
Ferric chloride	4.0	8.00
Pure alum + Nirmali seed extract	2.0 0.025	73.00 <sup>φ</sup>
Filter alum + Nirmali seed extract	6.6 0.025	4.50 <sup>φ</sup>
Ferric chloride + Nirmali seed extract	10.0 0.1	20.00 <sup>φ</sup>
Lime + Nirmali seed extract	5.0 0.01	1.75 <sup>φ</sup>
Pure alum + lime	1.0 + 2.5	36.62
Lime + ferric chloride	2.8 + 0.66	2.06
Pure alum + Ferric chloride	3.6 0.57	129.14
Pure alum + H <sub>2</sub> SO <sub>4</sub>	0.72 + 2.64	36.14

<sup>φ</sup> The cost of Nirmali seed powder was not taken into account, since the commercial cost is not available.

the cost comparison. One advantage of this combination is pH alteration is not much in this also. The only problem might be the presence of iron in the sludge.

In conclusion it can be said that this line of investigation could be further persuaded to obtain concentrated algal slurries for feeding to digestors after ascertaining the toxicity of chemicals to digestion. Since all the values used in the calculation are based on  $\frac{1}{2}$  hour sedimentation, it should be practicable to design a clarifloculator for concentrating the algae.

#### 4.4 SUMMARY

It is clear from the experiments on varying physical factors that no advantage is gained to any extent in algal removal, either by light or dark conditions, cold temperature conditions or exposure to sonic vibrations of bactericidal intensities. There was some removal under high pH conditions and this information was useful in later experiments. Among the chemical coagulants used singly or in combinations, the encouraging results obtained are summerized in the Table 14.

TABLE 14

## Chemicals Used and Per Cent Removal of Algae

Chemicals used	Dose of chemicals in mg/l	Per cent removal of algae in $\frac{1}{2}$ hour
Alum alone	500	85
Filter alum alone	1400	85
Lime alone	1000	70
Alum + Sulphuric acid	300 + (0.2 ml/l) (pH6)	85
Filter alum + Nirmali seed extract	1000 + 2	80

## CHAPTER V

## CONCLUSIONS

1. By changing physical environmental conditions there is no significant increase in concentration of algae in the sediment.
2. Under alkaline conditions there is considerable sedimentation of algae in  $\frac{1}{2}$  hour.
3. Among the chemicals used singly alum and ferric chloride gave similar removals with identical doses.
4. Filter alum (20 per cent pure alum) gave 85 per cent removal of algae in a dose of 1400 mg/l.
5. Combination of chemicals reduce the dose of individual chemicals. Among the combinations alum and sulphuric acid gave 85 per cent removal, reducing the alum dose from 500 to 300 mg/l.
6. 2 mg/l of nirmali seed extract reduced the filter alum dose from 1400 mg/l to 1000 mg/l with 80 per cent removal of algae.
7. From a cost analysis only the combination of lime and nirmali seed extract was least expensive followed by lime and ferric chloride.
8. Extract of crotalaria seed gave significant removals of turbidity but did not act on algal cells.

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